

11. SOURCES OF DIOXIN-LIKE PCBs

The purpose of this chapter is twofold: (1) to identify sources that release dioxin-like polychlorinated biphenyls (PCB) congeners into the environment and (2) to derive national estimates for releases from these sources in the United States. PCBs have been found in all media and all parts of the world. PCBs were produced in relatively large quantities for use in commercial products such as dielectrics, hydraulic fluids, plastics, and paints. They are no longer commercially produced in the United States, but continue to be released to the environment through the use and disposal of these products. PCBs may also be inadvertently produced as by-products during the manufacture of certain organic chemicals and also as products of the incomplete combustion of some waste materials.

11.1. GENERAL FINDINGS OF THE EMISSIONS INVENTORY

Table 11-1 provides a list of known or suspected dioxin-like PCB-emitting source categories in the United States. The source categories included in this table represent a compilation of source categories for which dioxin-like PCB congener, PCB Aroclor, or PCB congener group emission measurements have been reported in government, industry, and trade association reports; in conference proceedings and journal articles; and in comments submitted to the Agency on previous versions of this document. The intent of Table 11-1 is to clearly present those source categories and media (i.e., air, water, land, and products) for which available data are either adequate or inadequate for reliably quantifying emissions of dioxin-like PCBs.

Nationwide emission estimates for the United States inventory are presented in Table 11-2 (emissions to air, water, land, and product) for those source categories for which emission estimates can be reliably quantified (i.e., the category has been assigned a confidence rating of A, B, or C) (see Section 1.3 of this report for details on confidence ratings). Table 11-2 also lists, in the far right column, preliminary estimates of the potential magnitude of emissions from "unquantified" sources (i.e., sources assigned a confidence rating of D) in reference year 1995. Because of large uncertainties for these category D estimates, they are not included in the "quantitative inventory."

Releases of "old" dioxin-like PCBs (i.e., dioxin-like PCBs manufactured prior to the ban) to the environment can occur from ongoing use and disposal practices. Prior to

regulations enacted beginning in the late 1970s that limited the manufacture/use/disposal of PCBs, significant quantities of PCBs were released to the environment in association with (1) the manufacture of PCBs; (2) the manufacture of products containing PCBs; and (3) the use and disposal of products containing PCBs, as well as materials that may have been contaminated with trace levels of PCBs from prior PCB use or disposal. Following the ban on PCB production, releases from these first two categories ceased to exist. The third type of releases, those associated with product use and disposal, will continue in at least four ways:

- ! Products containing greater than 2 pounds of PCBs (e.g., dielectric fluids in transformers and large capacitors) are controlled by disposal regulations that have minimized environmental releases.
- ! Disposal of products containing small quantities of PCBs (e.g., small capacitors, fluorescent lighting fixtures) or trace quantities of PCBs (e.g., wastepapers) are subject to disposal as municipal solid waste but may result in some release to the general environment.
- ! Leaks and spills occur in still-in-service PCBs.
- ! PCBs are disposed of illegally.

No significant release of newly formed dioxin-like PCBs is occurring in the United States. Unlike CDD/CDFs, PCBs were intentionally manufactured in the United States in large quantities from 1929 until production was banned in 1977. Although it has been demonstrated that small quantities of dioxin-like PCBs can be produced during waste combustion, no strong evidence exists that the dioxin-like PCBs are produced in significant quantities as byproducts during combustion or chemical processes. The widespread occurrence of dioxin-like PCBs in the U.S. environment most likely reflects past releases associated with PCB production, use, and disposal. Further support for this finding is based on observations of reductions since the 1980s in PCB concentrations in Great Lakes sediment and other areas.

11.2 RELEASES OF COMMERCIAL PCBs

PCBs were commercially manufactured by the direct batch chlorination of molten biphenyl with anhydrous chlorine in the presence of a catalyst, followed by separation and

purification of the desired chlorinated biphenyl fractions. The degree of chlorination was controlled by the chlorine contact time in the reactor. Commercial PCBs production is believed to have been confined to 10 countries. Total PCBs produced worldwide since 1929 (i.e., the first year of known production) has been estimated to total 1.5-million metric tons. Initially, PCBs were primarily used as dielectric fluids in transformers. After World War II, PCBs found steadily increasing use as dielectric fluids in capacitors, as heat-conducting fluids in heat exchangers, and as heat-resistant hydraulic fluids in mining equipment and vacuum pumps. PCBs also were used in a variety of "open" applications (i.e, uses from which PCBs cannot be recollected) including: plasticizers, carbonless copy paper, lubricants, inks, laminating agents, impregnating agents, paints, adhesives, waxes, additives in cement and plaster, casting agents, dedusting agents, sealing liquids, fire retardants, immersion oils, and pesticides (DeVoogt and Brinkman, 1989).

PCBs were manufactured in the United States from 1929 until 1977. U.S. production peaked in 1970 with a volume of 39,000 metric tons. In 1971, Monsanto Corporation, the major U.S. producer, voluntarily restricted the sales of PCBs to all applications with the exception of "closed electrical systems," and annual production fell to 18,000 metric tons in 1974. Monsanto ceased PCB manufacture in mid-1977 and shipped the last inventory in October 1977. Regulations issued by EPA beginning in 1977, principally under the Toxic Substances Control Act (TSCA) (40 CFR 761), have strictly limited the production, import, use, and disposal of PCBs. The estimated cumulative production and consumption volumes of PCBs in the United States from 1930 to 1975 were 635,000 metric tons produced, 1,400 metric tons imported (primarily from Japan, Italy, and France), 568,000 metric tons sold in the United States; and 68,000 metric tons exported (Versar, 1976). The reliability of these values is + 5 percent and -20 percent (Versar, 1976).

Monsanto Corporation marketed technical grade mixtures of PCBs primarily under the trade name *Aroclor*. The Aroclors are identified by a four-digit numbering code in which the last two digits indicate the chlorine content by weight percent. The exception to this coding scheme is Aroclor 1016, which contains only mono- through hexachlorinated congeners with an average chlorine content of 41 percent. From 1957 until 1972, Monsanto also manufactured several blends of PCBs and polychlorinated terphenyls (PCTs) under the trade names Aroclor 2565 and Aroclor 4465; manufacture and sales volumes are

not available for these blends. Listed below are the percentages of total Aroclor production during the years 1957 to 1977 by Aroclor mixture as reported by Brown (1994).

| <u>Aroclor</u> | 1957-1977 U.S. Production (%) |
|----------------|-------------------------------------|
| 1016 | 12.88 |
| 1221 | 0.96 |
| 1232 | 0.24 |
| 1242 | 51.76 |
| 1248 | 6.76 |
| 1254 | 15.73 |
| 1260 | 10.61 |
| 1262 | 0.83 |
| 1268 | 0.33 |

The trade names of the major commercial PCB technical grade mixtures manufactured in other countries included *Clophen* (Germany), *Fenclor* and *Apirolito* (Italy), *Kanechlor* (Japan), *Phenoclor* and *Pyralene* (France), *Sovtel* (USSR), *Delor* and *Delorene* (Czechoslovakia), and *Orophene* (German Democratic Republic) (DeVoogt and Brinkman, 1989). The mixtures marketed under these trade names had similar chlorine content (by weight percent and average number of chlorines per molecule) to those of various Aroclors. Listed below are comparable mixtures in terms of chlorine content marketed under several trade names.

| <u>Aroclor</u> | <u>Clophen</u> | <u>Pyralene</u> | <u>Phenoclor</u> | <u>Fenclor</u> | <u>Kanechlor</u> |
|----------------|----------------|-----------------|------------------|----------------|------------------|
| 1232 | | 2000 | | | 200 |
| 1242 | A-30 | 3000 | DP-3 | 42 | 300 |
| 1248 | A-40 | | DP-4 | | 400 |
| 1254 | A-50 | | DP-5 | 54 | 500 |
| 1260 | A-60 | | DP-6 | 64 | 600 |

Major advances in analytical separation and resolution techniques during the 1980s and 1990s enabled various researchers to identify and quantify PCB congeners present in Aroclors, Clophens, and Kanechlors (Albro and Parker, 1979; Huckins et al., 1980; Albro et al., 1981; Duinker and Hillebrand, 1983; Kannan et al., 1987; Tanabe et al., 1987; Duinker et al., 1988; Schulz et al., 1989; Himberg and Sippola, 1990; Larsen et al., 1992; deBoer et al., 1993; and Schwartz et al., 1993). Schulz et al. (1989) were the first to identify and quantify all PCB congeners present in a series of Aroclors and Clophens. Frame (1995)

reported preliminary results of a nearly completed round robin study, one goal of which was to determine the distribution of all PCB congeners above 0.05 weight percent in various Aroclors (1221, 1016, 1242, 1260, and 1262) using 18 state-of-the-art gas chromatography/mass spectrometry (GC-MS) or electron capture detector (GC-ECD) systems.

Table 11-3 presents mean summary statistics on the concentrations of the dioxin-like PCBs in each mixture group (i.e., Aroclor 1248, Clophen A-40, and Kanechlor 400 are in one mixture group) reported by these researchers. Table 11-3 also presents calculation of the corresponding mean TEQ concentration of each congener in each mixture group as well as the total mean TEQ concentration in the mixture group. For each mixture group, the congeners detected were generally similar. There was, however, wide variability in the concentrations reported by some researchers for some congeners. Brown et al. (1995) compiled similar statistics using a somewhat different set of studies and derived significantly lower mean concentrations of some congeners in several Aroclors. Frame (1995) and Larsen (1995) attribute such differences either to potential limitations in the GC columns used by various researchers to separate similar eluting congeners or to actual differences in the congener concentrations in the Aroclor, Clophen, and Kanechlor lots analyzed by various research groups. Because of the wide variability in the reported results, the uncertainty associated with the mean concentrations reported in Table 11-3 is very large.

In the environment, PCBs also occur as mixtures of congeners, but their composition will differ from the commercial mixtures. This is because after release to the environment, the composition of PCB mixtures changes over time, through partitioning, chemical transformation, and preferential bioaccumulation (U.S. EPA, 1996g). Dioxin-like PCB congeners differ by up to one to two orders of magnitude in their water solubilities, vapor pressures, K_{ow} values, and Henry's Law constants. Thus, although all the dioxin-like PCB congeners are poorly soluble in water and have very low vapor pressures, they will volatilize and leach at different rates. Similarly, because the congeners differ somewhat in their rates of biodegradation, bioaccumulation, and photodegradation, the congener patterns found in environmental media and biota will vary from those found in commercial mixtures.

Although environmental mixtures are often characterized in terms of Aroclors, this characterization can be both imprecise and inappropriate. Qualitative and quantitative errors can arise from judgements in comparing GC/MS peaks for a sample with the characteristic peak patterns for different Aroclors, particularly for environmentally altered patterns (U.S. EPA, 1996g). For the same reason, it can be both imprecise and inappropriate to infer concentrations of dioxin-like PCB congeners in an environmental sample based on characterization of the sample's Aroclor content and knowledge of the dioxin-like congener content in the commercial Aroclor. Safe (1994) wrote, "Regulatory agencies and environmental scientists have recognized that the composition of PCBs in most environmental extracts does not resemble the compositions of the commercial product." Similarly, ATSDR (1993) stated, "It is important to recognize that the PCBs to which people may be exposed are likely to be different from the original PCB source because of changes in congener and impurity composition resulting from differential partitioning and transformation in the environment and differential metabolism and retention."

11.2.1. Approved PCB Disposal/Destruction Methods

In 1978, EPA began regulating the disposal of PCBs and PCB-contaminated waste under the TSCA, PL 94-469. The disposal regulations, published in the Code of Federal Regulations, 40 CFR, Part 761, state that the preferred disposal method is incineration at 1,200°C or higher. If the waste contains material that can not be destroyed by incineration, EPA clearance must be obtained to dispose of the waste in a chemical waste landfill, or in another approved manner.

The PCB disposal regulations describe disposal of three distinct types of PCB waste: PCBs, PCB articles (i.e., items containing PCBs), and PCB containers. Within these categories of PCB waste, further distinctions are made based on the PCB concentration in the waste. The acceptable disposal methods are based on the PCB concentrations in the specific waste to be destroyed. The acceptable disposal methods are: Annex I incinerators, high-efficiency boilers, Annex II chemical waste landfills, and other approved methods. The following subsections and Table 11-4 provide brief descriptions of these disposal methods. More complete descriptions of the specific methodologies are provided in the Code of Federal Regulations, 40 CFR, Part 761.

Approved Incinerators/High Efficiency Boilers - PCB Annex I incinerators must meet the specific technical standards and criteria listed in Annex I of EPA's PCB regulations. The minimum operating requirements for disposal of liquid wastes are 2 seconds at 1,200°C (2,190°F) with 3 percent excess oxygen (measured in the stack gas), or 1.5 seconds at 1,600°C (2,910°F) and 2 percent excess oxygen (measured in the stack gas). Monitoring requirements, approval conditions, and trial burn requirements are prescribed in Annex I. Commercial or industrial incinerators intending to destroy liquid PCB wastes must demonstrate compliance with the Annex I requirements through a comprehensive trial burn program. Annex I incinerators operating at optimum performance level should destroy 99.997 percent of liquid PCB waste with a resulting maximum emission factor of 0.03 grams per kilogram (g/kg).

Criteria for Annex I incinerators were established for the destruction of liquid PCB wastes; however, these incinerators also may be used for disposal of nonliquid PCB items (such as capacitors), provided that a destruction and removal efficiency of 99.9999 percent and a maximum emission factor of 0.001 g/kg are met.

High-efficiency boilers may be used to destroy PCBs and PCB-contaminated waste with PCB concentrations not exceeding 500 ppm. Conventional industrial and utility boilers may be designated as high-efficiency boilers, if they are operated under the prescribed combustion conditions defined in the PCB disposal regulations. The PCB regulations do not specify a minimum PCB destruction efficiency for high-efficiency boilers; however, EPA-approved boilers operated according to the regulations have reported destruction efficiencies in excess of 99.99 percent, with a corresponding maximum emission factor of 0.1 g/kg (U.S. EPA, 1987c).

Approved Chemical Waste Landfills - Approved chemical waste landfills can be used for the disposal of some, but not all, PCB wastes. PCB-contaminated materials acceptable for land disposal in an approved landfill include PCB mixtures (e.g., certain PCB-contaminated soil/solid debris, PCB-contaminated dredged materials, and PCB-contaminated municipal sewage sludge), PCB articles that cannot feasibly be incinerated (e.g., drained and flushed transformers), and drained PCB containers. EPA must issue written approval to landfill PCB articles other than transformers. PCB-contaminated materials not acceptable for land disposal in an approved landfill include nonliquid PCB mixtures in the form of contaminated soil, rags, or other solid debris, and sealed capacitors. Typically, PCBs

disposed in these landfills are placed in sealed containers, thereby, minimizing any PCB emissions.

Other Approved Disposal Methods - Other thermal and nonthermal destruction techniques may be approved by EPA Regional Administrators, if these processes can effect destruction of PCBs equivalent to that of incinerators or boilers. Subsequent to April 29, 1983, all other PCB disposal technologies (thermal and nonthermal) that are to be used in more than one EPA Region must be approved by EPA Headquarters. Examples of thermal technologies approved for commercial-scale use or for research and development projects include a pyrolysis process to treat contaminated soils, a fluid wall reactor, a cement kiln, a diesel engine, a steam-stripping operation, an aluminum melting furnace, and a molten salt process. Examples of approved nonthermal processes include chemical dechlorination processes, physical/chemical extraction techniques, and biological reduction methods. The physical/chemical techniques extract the PCBs from transformers or capacitors and concentrate them for disposal; they do not destroy the PCBs.

Emission Estimates - Table 11-5 lists the amounts of PCBs reported in EPA's Toxics Release Inventory (TRI) as transferred off-site for treatment, energy recovery, or disposal during the years 1988 through 1996. These quantities do not necessarily represent entry of PCBs into the environment. If it is assumed that all transferred PCBs are incinerated in high-efficiency boilers with a destruction and removal efficiency of 99.99 percent, then annual emissions of PCBs to air during 1988 and 1993 could have been as high as 264 kg and 31 kg, respectively. Because no stack testing data are available for dioxin-like PCBs, it is not possible to estimate what fraction of these potential PCB releases would have been the dioxin-like congeners.

11.2.2. Accidental Releases of In-Service PCBs

EPA banned PCB production and use in open systems in 1977. Subsequent to the 1977 ban, releases of commercially produced PCB to the environment (aside from minimal releases occurring during approved disposal and/or destruction) have been limited to accidental release of in-service PCBs (U.S. EPA, 1987c). Accidental releases are the result of leaks or spills during failure/breakage of an existing piece of PCB-containing equipment, or incomplete combustion occurring during accidental fires involving PCB-containing equipment. These two types of accidental releases are discussed in this section.

Leaks and Spills - PCBs that remain in active service at this time are those contained in "closed system" (i.e., those pieces of electrical equipment that completely enclose the PCBs and do not provide direct atmospheric access of the PCBs during normal use). This equipment includes PCB transformers, capacitors, voltage regulators, circuit breakers, and reclosures. With the exception of PCB transformers and probably small PCB capacitors, the majority of the PCB-containing electrical equipment in-service during 1981 was owned by the electrical utility industry. Approximately 70 percent of the estimated 140,000 PCB transformers in-service in 1981 were owned by nonutilities. No information was available on the relative distribution of small PCB capacitors (Versar, 1988).

The number of each of these items owned by the utility industry, the quantity of PCBs each contains, and an estimate of the annual quantity of PCBs leaked and/or spilled were investigated by the Edison Electric Institute and the Utility Solid Wastes Activity Group (EEI/USWAG) for EPA in 1981. The findings of this investigation were reported in a proposed modification to the PCB regulations (Federal Register, 1982a). The findings indicated that over 99 percent of the total quantity of PCBs contained in utility-owned electrical equipment in 1981 (73,700 metric tons) were in 40,000 PCB transformers (those containing > 500 ppm of PCBs) and large PCB capacitors (those containing > 3 lb of PCBs). An upper-bound estimate of the mass of PCBs that leached or spilled from this equipment in 1981 was 177 metric tons. Approximately 95 percent of the estimated releases were the result of leaks from large PCB capacitors (Federal Register, 1982a). Leaks/spills typically occur in transformers when the gasket joining the top to the body corrodes, tears, or physically fails. PCBs can then leak past this failed section and potentially spill onto the surrounding ground. PCB capacitors typically fail by rupturing, exposing the contained PCBs to the environment. Failure is caused by environmental and weathering effects (e.g., lightning) or material failures (e.g., metal fatigue).

As of mid-1988, the total population of in-service PCB transformers and large PCB capacitors was estimated to have decreased from 140,000 to 110,000 and from 3.3 million to 1.9 million, respectively (Versar, 1988). PCB transformers have normal operating lifetimes of 30 years and 40 years, respectively. The accelerated retirement rate over this 7-year period was attributed to EPA's PCB Electrical Use Rule (Federal Register, 1982b), which required the removal of 950 food/feed industry transformers by 1985 and removal of 1.1 million unrestricted-access large PCB capacitors by October 1988. In addition, EPA's

PCB Transformer Fires Rule (Federal Register, 1985b) required the removal by 1990 of 7,600 480-volt network transformers. More recent inventories of PCB-containing electrical equipment are not available. However, a recent Information Collection Request submitted by EPA to the Office of Management and Budget for information on uses, locations, and conditions of PCB electrical equipment estimated that there may be 150,000 owners of PCB-containing transformers used in industry, utilities, government buildings, and private buildings (Federal Register, 1997a). It is expected, and is demonstrated by the reported PCB transfers in TRI (see Table 11-5), that many owners of PCB electrical equipment have removed PCB-containing equipment to eliminate potential liability.

The proportion of spilled PCB that enters the atmosphere, runs off to surface water, or remains in or on the surface depends on a variety of factors including the porosity of the surface onto which the PCBs are spilled (concrete, soil), the PCB isomers that are spilled, ambient conditions (i.e., temperature, wind speed, precipitation), and the cleanup schedule. The number and diversity of factors affecting PCB emissions from spills and leaks make estimation of an emission factor difficult. A rough approximation of the annual amount that may be released to the environment from spills and leaks can be made using the release data reported by manufacturing facilities to EPA's TRI. Table 11-6 lists the amounts of PCBs reported in TRI to be released to the environment during 1988 through 1996. These data include emissions to the air, discharges to bodies of water, releases at the facility to land, as well as contained disposal into underground injection wells.

On the basis of TRI data, annual reported emissions of PCBs to air during 1988 and 1995 could have been as high as 2.7 kg and 0 kg, respectively. For purposes of deriving a preliminary rough estimate of potential releases of dioxin-like PCBs, it can be assumed that the ratio of TEQ to total PCB in the air emissions was 80:1-million (i.e., the average of the estimated mean TEQ contents for Aroclors 1242 and 1254 presented in Table 11-3). Based on this assumption, annual emissions of PCB TEQs in 1988 and 1995 could have been 0.2 and 0 grams, respectively. Similar assumptions for releases to water listed in Table 11-6 yield estimated TEQ emissions during 1988 and 1995 of 0.4 and 0 grams, respectively. For land, estimated TEQ emissions during 1988 and 1995 could have been 29 and 0 grams, respectively.

Accidental Fires - The available information is not adequate to support an estimate of potential annual releases of dioxin-like PCBs from accidental electrical equipment fires.

For fires involving PCB transformers or capacitors, the amount of PCBs released is dependent upon the extensiveness of the fire and the speed at which it is extinguished. A number of these fires are documented. A New York fire, involving 200 gallons of transformer fluid containing some 65 percent by weight PCBs, resulted in a release of up to 1,300 pounds of PCBs. A capacitor fire that burned uncontrolled for 2 hours in Sweden resulted in the destruction of 12 large utility capacitors containing an estimated 25 pounds of PCBs each, for a total potential release of 300 pounds. However, data are incomplete on the exact amount of PCBs released as a result of these two fires.

EPA has imposed reporting requirements to ensure that the National Response Center is informed immediately of fires involving PCB transformers (40 CFR 761). The recordkeeping requirements are used to document the use, location, and condition of PCB equipment. Responses are mandatory, but may be claimed by the submitter to be confidential information. The annual number of PCB transformer fires is estimated at approximately 20 per year; the number of PCB capacitor fires is unknown (U.S. EPA, 1987c). As these PCB items reach the end of their useful lives and are retired, their susceptibility to fires will be eliminated, and the overall number of PCB transformer and capacitor fires will be reduced.

11.2.3. Municipal Wastewater Treatment

EPA conducted the National Sewage Sludge Survey in 1988 and 1989 to obtain national data on sewage sludge quality and management. As part of this survey, EPA analyzed sludges from 175 publicly owned treatment works (POTWs) that employed at least secondary wastewater treatment for more than 400 analytes including 7 of the Aroclors. Sludges from 19 percent of the POTWs had detectable levels of at least one of the following Aroclors: 1248, 1254, or 1260; none of the other Aroclors were detected in any sample (detection limit was typically about 200 $\mu\text{g/kg}$ dry weight) (U.S. EPA, 1996a). Analyses were not performed for dioxin-like PCB congeners. The Aroclor-specific results of the survey are presented in Table 11-7. Gutenmann et al. (1994) reported similar results in a survey of sludges from 16 large U.S. cities for Aroclor 1260 content. At a detection limit of 250- $\mu\text{g/kg}$ (dry weight), Gutenmann et al. (1994) detected Aroclor 1260 at only one facility (4,600 $\mu\text{g/kg}$). These results indicate that PCBs are not likely to be formed at

POTWs, but rather are present because of disposal of PCB products or recirculation of previously disposed PCB.

Although PCBs, measured as Aroclors, were not commonly detected in sewage sludge at $\mu\text{g/kg}$ levels by U.S. EPA (1996a) and Gutenmann et al. (1994), the presence of dioxin-like PCB congeners at lower concentrations may be more common. Green et al. (1995) and Cramer et al. (1995) reported the results of analyses of 99 samples of sewage sludge for PCB congener numbers 77, 81, 126, and 169. The sludge samples were collected from 74 wastewater treatment plants across the United States during the summer of 1994. These data are summarized in Table 11-8. Results from all samples collected from the same facility were averaged by Green et al. (1995) and Cramer et al. (1995) to ensure that results were not biased towards the concentrations found at facilities from which more than one sample were collected. If all nondetected values are assumed to be zero, then the POTW mean $\text{TEQ}_p\text{-WHO}_{94}$ and $\text{TEQ}_p\text{-WHO}_{98}$ concentrations were 25.1 and 24.2 ng TEQ/kg (dry weight basis), respectively. If the nondetected values are set equal to the detection limits, then the POTW mean $\text{TEQ}_p\text{-WHO}_{94}$ and $\text{TEQ}_p\text{-WHO}_{98}$ concentrations were 25.2 and 24.3 ng TEQ/kg, respectively.

EPA recently analyzed samples of sewage sludge collected from a POTW in Ohio for all of the $\text{TEQ}_p\text{-WHO}_{94}$ and $\text{TEQ}_p\text{-WHO}_{98}$ dioxin-like PCB congeners, with the exception of PCB 81 (Battelle, 1999). The results of the analyses presented in the draft test report are listed in Table 11-9. The average TEQ content of the POTW sludge was 158 ng $\text{TEQ}_p\text{-WHO}_{94}/\text{kg}$ (141 ng $\text{TEQ}_p\text{-WHO}_{98}/\text{kg}$). Three PCB congeners, 77, 126, and 169, accounted for more than 97 percent of the total TEQ in each sample.

Approximately 5.4 million dry metric tons of sewage sludge are estimated by EPA to be generated annually in the United States based on the results of the 1988/1989 EPA National Sewage Sludge Survey (Federal Register, 1993b). Table 11-10 lists the volume of sludge disposed of annually by use and disposal practices. Table 11-10 also lists the estimated amount of dioxin-like PCB TEQs that may be present in sewage sludge and potentially be released to the environment. These values were estimated using the POTW mean $\text{TEQ}_p\text{-WHO}_{98}$ concentration calculated from the results reported by Green et al. (1995) and Cramer et al. (1995). Multiplying this TEQ concentration by the sludge volumes generated yields an annual potential total release of 101 g $\text{TEQ}_p\text{-WHO}_{98}$ for nonincinerated sludges. Of this 101 g $\text{TEQ}_p\text{-WHO}_{98}$, 1.7 grams enter commerce as a product for

distribution and marketing. The remainder is applied to land (51.1 grams) or is landfilled (48.2 grams).

These release estimates are assigned a confidence rating of B indicating high confidence in the production estimate and "medium" confidence in the emission factor estimates. The medium rating was based on the judgment that, although the 74 facilities tested by Green et al. (1995) and Cramer et al. (1995) may be reasonably representative of the variability in POTW technologies and sewage characteristics nationwide, the sample size was still relatively small, and not all dioxin-like PCB congeners were monitored.

11.3. CHEMICAL MANUFACTURING AND PROCESSING SOURCES

In the early 1980s, EPA investigated the extent of inadvertent generation of PCBs during the manufacture of synthetic organic chemicals (Hammerstrom et al., 1985). For example, phthalocyanine dyes and diarylide pigments were reported to contain PCBs in the mg/kg range. EPA subsequently issued regulations under TSCA (40 CFR 761.3) that banned the distribution in commerce of any products containing an annual average PCB concentration of 25 mg/kg (50 mg/kg maximum concentration at any time). In addition, EPA required manufacturers with processes inadvertently generating PCBs and importers of products containing inadvertently generated PCBs to report to EPA any process or import for which the PCB concentration is greater than 2 mg/kg for any resolvable PCB gas chromatographic peak.

11.4. COMBUSTION SOURCES

11.4.1 Municipal Solid Waste Incineration

Municipal solid waste incinerators have long been identified as potential PCB air emission sources. Stack gas concentrations of PCBs for three incinerators were reported in U.S. EPA (1987c), and the average test results yields an emission factor of 18 μg PCBs/kg refuse. Stack gas emissions of PCBs from the three incinerators were quantified without determining the incinerator's PCB destruction efficiency. The PCB content of various consumer paper products was analyzed as part of the study. This study indicates that paper products such as magazine covers and paper towels contained up to 139 micrograms of PCB per kilogram of paper ($\mu\text{g}/\text{kg}$). These levels, which were reported in 1981, were attributed to the repeated recycle of waste paper containing PCBs. For example,

carbonless copy paper manufactured prior to 1971 contained PCB levels as high as 7 percent. This copy paper then became a component of waste paper, which was recycled. The PCBs inevitably were introduced into other paper products, resulting in continued measurable levels in municipal refuse some 4 years after the PCB manufacturing ban was imposed. Refuse-derived fuel (RDF) manufactured from these paper products had PCB levels of 8,500 $\mu\text{g/kg}$, indicating that this fuel could be a source of atmospheric PCBs. Therefore, it was assumed in U.S. EPA (1987c) that municipal refuse does contain detectable levels of PCBs, and that some of these PCBs may enter the atmosphere when the refuse is incinerated.

Shane et al. (1990) analyzed fly ashes from five municipal solid waste (MSW) incinerators for PCB congener group content. Total PCB levels ranged from 99 to 322 $\mu\text{g/kg}$ in these ashes with the tri-, tetra-, and penta-congener groups occurring in the highest concentrations. Shane et al. (1990) also analyzed seven bottom ashes and eight bottom ash/fly ash mixtures for total PCB measured as Aroclor 1254. The detection limit for this Aroclor analysis was 5 $\mu\text{g/kg}$. Aroclor 1254 was detected in two of the seven bottom ash samples (26 and 8 $\mu\text{g/kg}$) and in five of the eight fly ash/bottom ash mixtures (range of 6 to 33 $\mu\text{g/kg}$).

The development of more sensitive analytical methodologies has enabled researchers in recent years to detect dioxin-like PCB congeners in the stack gases and fly ash from full-scale and pilot-scale MSW incinerators (Sakai et al., 1993a; Sakai et al., 1993b; Boers et al., 1993; Schoonenboom et al., 1993; Sakai et al., 1994). Similarly, the advances in analytical techniques have enabled researchers to determine that dioxin-like PCBs can be formed during the oxidative solid combustion phase of incineration presumably due to dimerization of chlorobenzenes. Laboratory-scale studies have also recently demonstrated that dioxin-like PCBs can be formed from heat treatment of fly ash in air (Schoonenboom et al., 1993; Sakai et al., 1994). However, the available data are not adequate to support development of a quantitative estimate of a dioxin-like PCB emission factor for this source category.

11.4.2. Industrial Wood Combustion

Emissions of PCB congener groups, not individual congeners, were measured during stack testing of two industrial wood burning facilities by the State of California Air

Resources Board (CARB, 1990e; 1990f). Table 11-11 presents the average of the congener group (i.e., mono- through decachlorobiphenyl) emission factors for these two facilities. No tetra- or more chlorinated congeners (i.e., the congener groups containing the dioxin-like PCBs) were detected at either facility at detection limits corresponding to emission factors in the low range of ng/kg of wood combusted.

In CARB (1990e), PCBs were measured in the emissions from two spreader stoker wood-fired boilers operated in parallel by an electric utility for generating electricity. The exhaust gas stream from each boiler is passed through a dedicated ESP after which the gas streams are combined and emitted to the atmosphere through a common stack. Stack tests were conducted both when the facility burned fuels allowed by existing permits and when the facility burned a mixture of permitted fuel supplemented by urban wood waste at a ratio of 70:30.

In CARB (1990f), PCBs were measured in the emissions from twin fluidized bed combustors designed to burn wood chips to generate electricity. The APCD system consisted of ammonia injection for controlling nitrogen oxides, and a multiclone and electrostatic precipitator for controlling particulate matter. During testing, the facility burned wood wastes and agricultural wastes allowed by existing permits.

11.4.3. Medical Waste Incineration

As discussed in Section 3.3, EPA recently issued nationally applicable emission standards and guidelines for medical waste incinerators (MWI) that address CDD/CDF emissions. Although PCBs are not addressed in these regulations, the data base of stack test results at MWIs compiled for this rulemaking does contain limited data on PCB congener group emission factors. Data are available for two MWIs lacking add-on APCD equipment and for two MWIs with add-on APCD equipment in place. The average congener group emission factors derived from these test data are presented in Table 11-12. Because data are available for only 4 of the estimated 2,400 facilities that make up this industry and because these data do not provide congener-specific emission factors, no national estimates of total PCB or dioxin-like PCB emissions are being made at this time.

11.4.4. Tire Combustion

Emissions of PCB congener groups, not individual congeners, were measured during stack testing of a tire incinerator by the State of California Air Resources Board (CARB, 1991a). The facility consists of two excess air furnaces equipped with steam boilers to recovery the energy from the heat of combustion. Discarded whole tires were fed to the incineration units at rates ranging from 2,800 to 5,700 kg/hr during the 3 testing days. The furnaces are equipped to burn natural gas as auxiliary fuel. The steam produced from the boilers drives electrical turbine generators that produce 14.4 megawatts of electricity. The facility is equipped with a dry acid gas scrubber and fabric filter for the control of emissions prior to exiting the stack. Table 11-13 presents the congener group (i.e., mono- through decachlorobiphenyl) emission factors for this facility. The emission factor for the total of the tetra- through hepta-chlorinated congener groups is about 1.2 $\mu\text{g/kg}$ of tire processed.

EPA estimated that approximately 0.50 million metric tons of tires were incinerated in 1990 in the United States (U.S. EPA, 1992a). This production estimate is given a medium confidence rating, because it is based on both published data and professional judgment. The use of scrap tires as a fuel increased significantly during the late 1980s; however, no quantitative estimates were provided in U.S. EPA (1992a) for this period. In 1990, 10.7 percent of the 242 million scrap tires generated were burned for fuel. This percentage is expected to continue to increase (U.S. EPA, 1992a). Of the tires burned for energy recovery purposes, pulp and paper facilities used approximately 46 percent; cement kilns, 23 percent; and one tire-to-energy facility, 19 percent (U.S. EPA, 1997b).

If it is assumed that 500 million kg of discarded tires are incinerated annually in the United States, then, using the sum of the average emission factors for the total tetra- through heptachlorinated congener groups (1.2 $\mu\text{g/kg}$ tire processed) derived from stack data from the one tested facility, yields a total emission of 610 g/yr. However, it is not known what fraction of this emission is dioxin-like PCBs.

11.4.5. Cigarette Smoking

Using high-resolution mass spectrometry, Matsueda et al. (1994) analyzed tobacco from 20 brands of commercially available cigarettes collected in 1992 from Japan, the

United States, Taiwan, China, the United Kingdom, Germany, and Denmark for the PCB congeners 77, 126, and 169. Table 11-14 presents the results of the study.

However, no studies have been reported which examined the tobacco smoke for the presence of these congeners. Thus, it is not known whether the PCBs present in the tobacco are destroyed or volatilized during combustion, or whether PCBs are formed during combustion. The combustion processes operating during cigarette smoking are complex and could be used to support either of these potential mechanisms. As reported by Guerin et al. (1992), during a puff, gas phase temperatures reach 850°C at the core of the firecone, and solid phase temperatures reach 800°C at the core and 900°C or greater at the char line. Thus, temperatures are sufficient to cause at least some destruction of CDD/CDFs initially present in the tobacco. Both solid and gas phase temperatures rapidly decline to 200 to 400°C within 2 mm of the char line. Formation of dioxin-like PCBs has been reported in combustion studies with other media in this temperature range (Sakai et al., 1994). However, it is known that a process likened by Guerin et al. (1992) to steam distillation takes place in the region behind the char line because of high localized concentrations of water and temperatures of 200 to 400°C. At least 1,200 tobacco constituents (e.g., nicotine, n-paraffin, some terpenes) are transferred intact from the tobacco into the smoke stream by distillation in this area, and it is plausible that PCBs present in the unburned tobacco would be subject to similar distillation.

In 1995, approximately 487 billion cigarettes were consumed in the United States and by U.S. Armed Forces personnel stationed overseas. Per capita U.S. cigarette consumption in 1995, based on total U.S. population aged 16 and over, declined to 2,415 from a record high of 4,345 in 1963. In 1987, approximately 575 billion cigarettes were consumed domestically (The Tobacco Institute, 1995; USDA, 1997).

A preliminary rough estimate of potential emissions of dioxin-like PCBs can be made using the following assumptions: (1) the average TEQ_p-WHO₉₈ content of seven brands of U.S. cigarettes reported by Matsueda et al. (1994), 0.64 pg/pack (or 0.032 pg/cigarette) is representative of cigarettes smoked in the United States; (2) dioxin-like PCBs are neither formed nor destroyed, and the congener profile reported by Matsueda et al. (1994) is not altered during combustion of cigarettes; and (3) all dioxin-like PCBs contributing to the TEQ are released from the tobacco during smoking. Based on these assumptions, the calculated

annual emissions would be 0.018 g TEQ_p-WHO₉₈ and 0.016 g TEQ_p-WHO₉₈ for reference years 1987 and 1995, respectively.

11.4.6. Sewage Sludge Incineration

U.S. EPA (1996f) derived an emission factor of 5.4 μ g of total PCBs per kg of dry sludge incinerated. This emission factor was based on measurements conducted at five multiple hearth incinerators controlled with wet scrubbers. In 1992, approximately 199 sewage sludge incineration facilities combusted 0.865 million metric tons of dry sewage sludge (Federal Register, 1993b). Given this mass of sewage sludge incinerated, the estimated annual release of total PCBs to air annually is 4,670 g. However, it is not known what fraction of this annual emission is dioxin-like PCBs.

EPA recently conducted stack testing at a sewage sludge incinerator in Ohio (Battelle, 1999) for all of the TEQ_p-WHO₉₄ and TEQ_p-WHO₉₈ dioxin-like PCB congeners with the exception of PCB 81. The results of the analyses (ng/dscm) presented in the draft test report are listed in Table 11-15. The average TEQ content of the stack gas was 0.119 ng TEQ_p-WHO₉₄/dscm (0.106 ng TEQ_p-WHO₉₈/dscm). Three PCB congeners, 77, 126, and 169, accounted for more than 97 percent of the total TEQ in each sample.

11.4.7. Backyard Barrel Burning

In many rural areas of the United States, disposal of residential solid waste may take place via open backyard burning in barrels or similar homemade devices. Although no national statistics on the prevalence of this practice have been reported, the results of a telephone survey conducted in the early 1990s of residents in five central Illinois counties indicate that about 40 percent of the residents in a typical rural Illinois county burn household waste. The survey also found that, on average, those households that burn waste dispose of approximately 63 percent of their household waste through burning in barrels (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).

The low combustion temperatures and oxygen-starved conditions associated with this method may result in incomplete combustion and increased pollutant emissions (Lemieux, 1997). EPA's Control Technology Center, in cooperation with the New York State Departments of Health (NYSDOH) and Environmental Conservation (NYSDEC), recently conducted a study to examine, characterize, and quantify emissions from the

simulated open burning of household waste materials in barrels (Lemieux, 1997). A representative waste to be burned was prepared based on the typical percentages of various waste materials disposed by New York State residents (i.e., nonhazardous recyclers); hazardous wastes (i.e., chemicals, paints, oils, etc.) were not included in the test waste. A variety of compounds, including dioxin-like PCBs, were measured in the emissions from the simulated open burning. The measured TEQ emission factors for waste, which had not been separated for recycling purposes, were $1.02\text{E-}2 \mu\text{g TEQ}_p\text{-WHO}_{94}/\text{kg}$ of waste burned and $5.26\text{E-}3 \mu\text{g TEQ}_p\text{-WHO}_{98}/\text{kg}$ (see Table 11-16).

The limited emission factor and activity level data available were judged inadequate for developing national emission estimates that could be included in the national inventory. The number of households nationwide burning waste in barrels and the total amount and variability of burned waste is unknown. The representativeness of the trash and burning conditions used in the experiments to conditions nationwide are unknown. However, combining the emission factor of $5.26\text{E-}3 \mu\text{g TEQ}_p\text{-WHO}_{98}/\text{kg}$ of waste burned with the following information/assumptions, allows a preliminary order of magnitude estimate to be made of potential national dioxin-like PCB TEQ emissions from backyard household trash burning.

- Forty percent of the rural population in the United States are assumed to burn their household waste in a barrel (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).
- On average, each U.S. citizen generates 3.72 pounds of solid waste (excluding yard waste) per day (or 616 kg/person-year) (U.S. EPA, 1996b).
- On average, for those individuals burning household waste, approximately 63 percent of waste generated are burned (i.e., 63 percent of 616 kg/person-year = 388 kg/person-year) (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).
- In 1992, 51.8 million people lived in nonmetropolitan areas (U.S. DOC, 1997).

$$\begin{aligned} \text{Emissions} &= (51.8 \times 10^6 \text{ people})(40\%)(388 \text{ kg/person-yr})(5.26\text{E-}3 \mu\text{g TEQ}_p\text{-WHO}_{98}/\text{kg})(10^{-6} \text{ g}/\mu\text{g}) \\ &= 42.3 \text{ g TEQ}_p\text{-WHO}_{98}/\text{yr} \quad (82.1 \text{ g TEQ}_p\text{-WHO}_{94}/\text{yr}) \end{aligned}$$

11.4.8. Petroleum Refining Catalyst Regeneration

As discussed in Section 5.3, regeneration of spent catalyst used in catalytic reforming to produce high-octane reformates is a potential source of CDD/CDF air emissions. In 1998, emissions from the caustic scrubber used to treat gases from the external catalyst regeneration unit of a refinery in California were tested for CDD/CDFs, as well as PCB congener groups (CARB, 1999). This facility uses a continuous regeneration process. The reactor is not taken off line during regeneration; rather, small amounts of catalyst are continuously withdrawn from the reactor and are regenerated. The emissions from the regeneration unit are neutralized by a caustic scrubber before being vented to the atmosphere. The catalyst recirculation rate during the three tests ranged from 733 to 1,000 lb/hr.

All PCB congener groups were detected in each of the three samples collected. The average congener group emission factors in units of ng per barrel of reformer feed are presented in Table 11-17. The total PCB emission factor was 118 ng/barrel. This emission factor assumes that emissions are proportional to reforming capacity; emission factors may be more related to the amount of coke burned, APCD equipment present, and/or other process parameters.

Because emissions data are available for only one U.S. petroleum refinery (which represents less than 1 percent of the catalytic reforming capacity at U.S. refineries) and because these data do not provide congener-specific emission factors, no national estimates of total PCB or dioxin-like PCB emissions are being made at this time.

11.5. NATURAL SOURCES

11.5.1. Biotransformation of Other PCBs

Studies show that under anaerobic conditions, biologically mediated reductive dechlorination to less chlorinated congeners, followed by slow anaerobic and/or aerobic biodegradation, is a major pathway for destruction of PCBs in the environment. Research reported to date and summarized below indicates that biodegradation should result in a net decrease rather than a net increase in the environmental load of dioxin-like PCBs.

Laboratory studies (e.g., Bedard et al., 1986; Pardue et al., 1988; Larsson and Lemkemeier, 1989; Hickey, 1995; and Schreiner et al., 1995) have revealed that more than two dozen strains of aerobic bacteria and fungi, which are capable of degrading most PCB

congeners with five or fewer chlorines, are widely distributed in the environment. Many of these organisms are of the genus *Pseudomonas* or the genus *Alcaligenes*. The major metabolic pathway involves addition of O₂ at the 2,3-position by a dioxygenase enzyme with subsequent dehydrogenation to the catechol followed by ring cleavage. Several bacterial strains have been shown to possess a dioxygenase enzyme that attacks the 3,4-position.

However, only a few strains have demonstrated the ability to degrade hexa- and more chlorinated PCBs. The rate of aerobic biodegradation decreases with increasing chlorination. The half-lives for biodegradation of tetra-PCBs in fresh surface water and soil are 7 to 60+ days and 12 to 30 days, respectively. For penta-PCBs and higher chlorinated PCBs, the half-lives in fresh surface water and soil are likely to exceed 1 year. PCBs with all or most chlorines on one ring and PCBs with fewer than two chlorines in the ortho position tend to degrade more rapidly. For example, Gan and Berthouex (1994) monitored over a 5-year period the disappearance of PCB congeners applied to soil with sewage sludge. Three of the tetra- and pentachlorinated dioxin-like PCBs (IUPAC Nos. 77, 105, and 118) followed a first-order disappearance model with half-lives ranging from 43 to 69 months. A hexa-substituted congener (IUPAC No. 167) and a hepta-substituted congener (IUPAC No. 180) showed no significant loss over the 5-year period.

Until recent years, little investigation focused on anaerobic microbial dechlorination or degradation of PCBs even though most PCBs eventually accumulate in anaerobic sediments (Abramowicz, 1990; Risatti, 1992). Environmental dechlorination of PCBs via losses of meta and para chlorines has been reported in field studies for freshwater, estuarine, and marine anaerobic sediments including those from the Acushnet Estuary, the Hudson River, the Sheboygan River, New Bedford Harbor, Escambia Bay, Waukegan Harbor, the Housatonic River, and Woods Pond (Brown et al., 1987; Rhee et al., 1989; Van Dort and Bedard, 1991; Abramowicz, 1990; Bedard et al., 1995; and Bedard and May, 1996). The altered PCB congener distribution patterns found in these sediments (i.e., different patterns with increasing depth or distance from known sources of PCBs) have been interpreted as evidence that bacteria may dechlorinate PCBs in anaerobic sediment.

Results of laboratory studies reported recently confirm anaerobic degradation of PCBs. Chen et al. (1988) found that "PCB-degrading" bacteria from the Hudson River could significantly degrade the mono-, di-, and tri-PCB components of a 20 ppm Aroclor

1221 solution within 105 days. These congener groups make up 95 percent of Aroclor 1221. No degradation of higher chlorinated congeners (present at 30 ppb or less) was observed, and a separate 40-day experiment with tetra-PCB also showed no degradation.

Rhee et al. (1989) reported degradation of mono- to penta-substituted PCBs in contaminated Hudson River sediments held under anaerobic conditions in the laboratory (N_2 atmosphere) for 6 months at 25°C. Amendment of the test samples with biphenyl resulted in greater loss of PCB. No significant decreases in the concentrations of the more highly chlorinated (i.e., more than five chlorines) were observed. No evidence of degradation was observed in samples incubated in CO_2/H_2 atmospheres. Abramowicz (1990) hypothesized that this result could be an indication that, in the absence of CO_2 , a selection is imposed favoring organisms capable of degrading PCBs to obtain CO_2 and/or low molecular weight metabolites as electron receptors.

Risatti (1992) examined the degradation of PCBs at varying concentrations (10,000 ppm, 1,500 ppm, and 500 ppm) in the laboratory with "PCB-degrading" bacteria from Waukegan Harbor. After 9 months of incubation at 22°C, the 500 ppm and 1,500 ppm samples showed no change in PCB congener distributions or concentrations, thus indicating a lack of degradation. Significant degradation was observed in the 10,000 ppm sediment with at least 20 congeners ranging from TrCBs to PeCBs showing decreases.

Quensen et al. (1988) also demonstrated that microorganisms from PCB-contaminated sediments (Hudson River) dechlorinated most tri- through hexa-PCBs in Aroclor 1242 under anaerobic laboratory conditions. The Aroclor 1242 used to spike the sediment contained predominantly tri- and tetra-PCBs (85 mole percent). Three concentrations of the Aroclor, corresponding to 14-, 140-, and 700-ppm on a sediment dry-weight basis, were used. Dechlorination was most extensive at the 700-ppm test concentration; 53 percent of the total chlorine were removed in 16 weeks, and the proportion of TeCBs through HxCBs decreased from 42 to 4 percent. Much less degradation was observed in the 140-ppm sediment, and no observable degradation was found in the 14-ppm sediment. These results and those of Risatti (1992) suggest that the organism(s) responsible for this dechlorination may require relatively high levels of PCB as a terminal electron acceptor to maintain a growing population.

Quensen et al. (1990) reported that dechlorination of 500-ppm spike concentrations of Aroclor 1242, 1248, 1254, and 1260 by microorganisms from PCB-contaminated

sediments in the Hudson River and Silver Lake occurred primarily at the meta- and para-positions; ortho-substituted mono- and di-PCBs increased in concentration. Significant decreases over the up to 50-week incubation period were reported for the following dioxin-like PCBs: 156, 167, 170, 180 and 189. Of the four dioxin-like TeCBs and PeCBs detected in the Aroclor spikes (i.e., IUPAC Nos. 77, 105, 114, and 118), all decreased significantly in concentration, with the possible exception of PeCB 114 in the Aroclor 1260-spiked sediment.

Nies and Vogel (1990) reported similar results with Hudson River sediments incubated anaerobically and enriched with acetone, methanol, or glucose. Approximately 300 ppm of Aroclor 1242 (31-mole percent TeCBs, 7-mole percent PeCBs, and 1-mole percent HxCBs) were added to the sediments prior to incubation for 22 weeks under an N₂ atmosphere. Significant dechlorination was observed, with dechlorination occurring primarily at the meta- and para-positions on the more highly chlorinated congeners (i.e., TeCBs, PeCBs, and HxCBs), resulting in the accumulation of less-chlorinated, primarily ortho-substituted mono- through tri-substituted congeners. No significant dechlorination was observed in the control samples (i.e., samples containing no added organic chemical substrate and samples that were autoclaved).

Bedard and May (1996) also reported similar findings in the sediments of Woods Pond, believed contaminated with Aroclor 1260. Significant decreases in the sediment concentrations of PCBs 118, 156, 170, and 180 (relative to their concentrations in Aroclor 1260) were observed. No increases or decreases were reported for the other dioxin-like PCBs.

Bedard et al. (1995) demonstrated that it is possible to stimulate substantial microbial dechlorination of the highly chlorinated PCB mixture Aroclor 1260 *in situ* with a single addition of 2,6-dibromobiphenyl. Bedard et al. (1995) added 365 g of 2,6-dibromobiphenyl to 6-foot-diameter submerged caissons containing 400-kg sediment (dry weight) and monitored the change in PCB congener concentrations for a period of 1 year. At the end of the observation period, the hexa- through monochlorinated PCBs decreased 74 percent in the top of the sediment and 69 percent in the bottom. The average number of chlorines per molecule dropped 21 percent from 5.83 to 4.61, with the largest reduction observed in meta-chlorines (54 percent reduction) followed by para-chlorines (6 percent).

The dechlorination stimulated by 2,6-dibromobiphenyl selectively removed meta-chlorines positioned next to other chlorines.

The findings of these latter studies are significant, because removal of meta- and para-chlorines from the dioxin-like PCBs should reduce their toxicity and bioaccumulative potential and also form less chlorinated congeners that are more amenable to aerobic biodegradation.

Van Dort and Bedard (1991) reported the first experimental demonstration of biologically mediated ortho-dechlorination of a PCB and stoichiometric conversion of that PCB congener (2,3,5,6-TeCB) to less chlorinated forms. In that study, 2,3,5,6-TeCB was incubated under anaerobic conditions with unacclimated methanogenic pond sediment for 37 weeks, with reported dechlorination to 2,5-DCB (21 percent); 2,6-DCB (63 percent); and 2,3,6-TrCB (16 percent).

11.5.2. Photochemical Transformation of Other PCBs

Photolysis and photo-oxidation may be major pathways for destruction of PCBs in the environment. Research reported to date and summarized below indicates that ortho-substituted chlorines are more susceptible to photolysis than are meta- and para-substituted congeners. Thus, photolytic formation of more toxic dioxin-like PCBs may occur. Oxidation by hydroxyl radicals, however, apparently occurs preferentially at the meta- and para-positions thus resulting in a net decrease rather than a net increase in the environmental load of dioxin-like PCBs.

Based on the data available in 1983, Leifer et al. (1983) concluded that all PCBs, especially the more highly chlorinated congeners and those that contain two or more chlorines in the ortho-position, photodechlorinate. In general, as the chlorine content increases, the photolysis rate increases. More recently, Lepine et al. (1992) exposed dilute solutions (4 ppm) of Aroclor 1254 in cyclohexane to sunlight for 55 days in December and January. Congener-specific analysis indicated that the amounts of many higher chlorinated congeners, particularly mono-ortho-substituted congeners decreased, while those of some lower chlorinated congeners increased. The results for the dioxin-like PCBs indicated a 43.5 percent decrease in the amount of PeCB 114; a 73.5 percent decrease in the amount of HxCB 156; and a 24.4 percent decrease in the amount of HxCB 157. However, TeCB 77 and PeCB 126 (the most toxic of the dioxin-like PCB congeners), which were not

detected in unirradiated Aroclor 1254, represented 2.5 percent and 0.43 percent, respectively, of the irradiated mixture.

With regard to photo-oxidation, Atkinson (1987) and Leifer et al. (1983), using assumed steady-state atmospheric OH concentrations and measured oxidation rate constants for biphenyl and monochlorobiphenyl, estimated atmospheric decay rates and half-lives for gaseous-phase PCBs. Atmospheric transformation was estimated to proceed most rapidly for those PCB congeners containing either a small number of chlorines or those containing all or most of the chlorines on one ring. Kwok et al. (1995) extended the work of Atkinson (1987) by measuring the OH radical reaction rate constants for 2,2'-, 3,3'-, and 3,5-dichlorobiphenyl. These reaction rate constants, when taken together with the Atkinson's measurements for biphenyl and monochlorobiphenyl and the estimation method described in Atkinson (1991), were used to generate more reliable estimates of the gas-phase OH radical reaction rate constants for the dioxin-like PCBs. The persistence of the PCB congeners increases with increasing degree of chlorination. Table 11-18 presents these estimated rate constants and the corresponding tropospheric lifetimes and half-lives.

Sedlak and Andren (1991) demonstrated in laboratory studies that OH radicals, generated with Fenton's reagent, rapidly oxidized PCBs (i.e., 2-mono-PCB and the DiCBs through PeCBs present in Aroclor 1242) in aqueous solutions. The results indicated that the reaction occurs via addition of a hydroxyl group to one nonhalogenated site; reaction rates are inversely related to the degree of chlorination of the biphenyl. The results also indicated that meta- and para-sites are more reactive than ortho-sites due to steric hindrance effects. Based upon their kinetic measurements and reported steady-state aqueous system OH concentrations or estimates of OH radical production rates, Sedlak and Andren (1991) estimated environmental half-lives for dissolved PCBs (mono-through octa-PCB) in fresh surface water and in cloud water to be 4 to 11 days and 0.1 to 10 days, respectively.

11.6. PAST USE OF COMMERCIAL PCBS

An estimated 1.5 million metric tons of PCBs were produced worldwide (DeVoogt and Brinkman, 1989). Slightly more than one-third of these PCBs (568,000 metric tons) were used in the United States (Versar, 1976). Although the focus of this section is on reservoir sources of PCBs within the United States, it is necessary to note that the use and

disposal of PCBs in many countries, coupled with the persistent nature of PCBs, have resulted in their movement and presence throughout the global environment. The ultimate sink of most PCBs released to the environment will be aquatic sediments. Currently, however, large quantities of PCBs are estimated to be circulating between the air and water environments or are present in landfills and dumps, some of which may offer the potential for re-release of PCBs into the air. Tanabe (1988) presented a global mass balance for PCBs that indicated that as of 1985, 20 percent of the total PCBs produced were present in seawater, whereas only 11 percent were in sediments. (See Table 11-19.) Nearly two-thirds of total global PCB production was estimated by Tanabe (1988) to still be in use in electrical equipment or to be present in landfills and dumps.

As discussed in Section 11.2, an estimated 568,000 metric tons of PCBs were sold in the United States during the period 1930-1975 (Versar, 1976). Table 11-20 presents annual estimates of domestic sales by year for each Aroclor during the period 1957-1974. Estimates of PCB usage in the United States by usage category during the period 1930-1975 are presented in Table 11-21. Prior to voluntary restrictions by Monsanto Corporation in 1972 on sales for uses other than "closed electrical systems," approximately 13 percent of the PCBs were used in "semi-closed applications," and 26 percent were used in "open-end applications." Most of this usage of PCBs for "semi-closed" and "open-end" applications occurred between 1960 and 1972 (Versar, 1976).

Table 11-22 presents estimates of the amounts of individual Aroclors that were released to the environment (i.e., to water, air, or soil) during the period 1930-1974. Because detailed usage data were not available for the period 1930-1957, Versar (1976) assumed that the usage pattern for this period followed the average pattern for the period 1957-1959. The basic assumptions used by Versar (1976) in deriving these estimates were that 5 percent of the PCBs used in "closed electrical systems" were released; 60 percent of the PCBs used in "semi-closed applications" were released; 25 percent of the PCBs used for plasticizers were released; and 90 percent of PCBs used for miscellaneous industrial uses had escaped. The reliability of these release estimates was assumed to be ± 30 percent (Versar, 1976).

In addition to these estimates of direct releases to the environment, Versar (1976) estimated that 132,000 metric tons of PCBs were landfilled. This total was comprised of 50,000 metric tons from capacitor and transformer production wastes, 36,000 metric tons

from disposal of obsolete electrical equipment, and 46,000 metric tons from disposal of material from "open-end applications." An additional 14,000 metric tons of PCBs, although still "in service" in various "semi-closed" and "open-end" applications in 1976 were estimated to ultimately be destined for disposal in landfills.

An estimated 4,574 kg of $TEQ_p\text{-WHO}_{98}$ were released directly to the U.S. environment during the period 1930-1977 (See Table 11-23). These estimates are based on the Aroclor release estimates presented in Table 11-22 and the mean $TEQ_p\text{-WHO}_{98}$ concentrations in Aroclors that were presented in Table 11-3.

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Table 11-1. List of Known and Suspected Source Categories for Dioxin-like PCBs

| Emission Source Category | Source Categories for Which Emissions Can Be Reliably Quantified | | | | | | | | Source Categories for Which Emissions Cannot Be Reliably Quantified | | | | | | | |
|--|--|------|-------|------|------|------|---------|------|---|------|-------|------|------|------|---------|------|
| | Air | | Water | | Land | | Product | | Air | | Water | | Land | | Product | |
| | 1995 | 1987 | 1995 | 1987 | 1995 | 1987 | 1995 | 1987 | 1995 | 1987 | 1995 | 1987 | 1995 | 1987 | 1995 | 1987 |
| Releases of Commercial PCBs | | | | | | | | | | | | | | | | |
| Approved disposal | | | | | | | NA | NA | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NA | NA |
| Accidental releases | | | | | | | NA | NA | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NA | NA |
| Municipal Wastewater Treatment | | | | | | | | | | | | | | | | |
| Nonincinerated sludge | | | | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | |
| Chemical Manufacturing/Processing Sources | | | | | | | | | | | | | | | | |
| Dyes and pigments | | | | | | | | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Combustion Sources | | | | | | | | | | | | | | | | |
| Municipal waste incineration | | | | | | | NA | NA | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NA | NA |
| Industrial wood combustion | | | | | | | NA | NA | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NA | NA |
| Medical waste incineration | | | | | | | NA | NA | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NA | NA |
| Tire combustion | | | | | | | NA | NA | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NA | NA |
| Cigarette combustion | | | NA | NA | NA | NA | NA | NA | ✓ | ✓ | NA | NA | NA | NA | NA | NA |
| Sewage sludge incineration | | | | | | | NA | NA | ✓ | ✓ | ✓ | ✓ | ✓ | | NA | NA |
| Backyard barrel burning | | | NA | NA | | | NA | NA | ✓ | ✓ | NA | NA | ✓ | ✓ | NA | NA |

NA = This source category is not expected to generate releases to this environmental medium.

Table 11-2. Quantitative Inventory of Dioxin-Like PCB TEQ_p-WHO₉₈ Releases in the United States

| Emission Source Category | Quantitative Inventory Confidence Rating ^a Reference Year 1995 | | | Quantitative Inventory Confidence Rating ^a Reference Year 1987 | | | Preliminary Estimate for 1995 ^b |
|--|---|---|---|---|---|---|--|
| | A | B | C | A | B | C | |
| Releases (g TEQ _p -WHO ₉₈ /yr) to Air | | | | | | | |
| Releases of Commercial PCBs Approved disposal | | | | | | | |
| Accidental releases | | | | | | | 0 |
| Municipal Sludge Disposal Nonincinerated sludge | | | | | | | |
| Chemical Manufacturing/Processing Sources Dyes and pigments | | | | | | | |
| Combustion Sources | | | | | | | |
| Municipal waste incineration | | | | | | | |
| Industrial wood combustion | | | | | | | |
| Medical waste incineration | | | | | | | |
| Tire combustion | | | | | | | |
| Cigarettes | | | | | | | 0.016 |
| Sewage sludge incineration | | | | | | | |
| Backyard barrel burning | | | | | | | 42.3 |
| Petroleum refining catalyst regeneration | | | | | | | |
| Total Quantified Releases to Air ^c | 0 | 0 | 0 | 0 | 0 | 0 | 42.3 |
| Releases (g TEQ _p -WHO ₉₈ /yr) to Water | | | | | | | |
| Releases of Commercial PCBs Approved disposal | | | | | | | |
| Accidental releases | | | | | | | 0 |
| Municipal Sludge Disposal Nonincinerated sludge | | | | | | | |
| Chemical Manufacturing/Processing Sources Dyes and pigments | | | | | | | |
| Combustion Sources | | | | | | | |
| Municipal waste incineration | | | | | | | |
| Industrial wood combustion | | | | | | | |
| Medical waste incineration | | | | | | | |
| Tire combustion | | | | | | | |
| Sewage sludge incineration | | | | | | | |
| Total Quantified Releases to Water ^c | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Releases (g TEQ _p -WHO ₉₈ /yr) to Land | | | | | | | |
| Releases of Commercial PCBs Approved disposal | | | | | | | |
| Accidental releases | | | | | | | 0 |
| Municipal Sludge Disposal Nonincinerated sludge | 51.1 | | | 51.1 | | | |
| Chemical Manufacturing/Processing Sources Dyes and pigments | | | | | | | |

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Table 11-2. Quantitative Inventory of Dioxin-Like PCB TEQ_p-WHO₉₈ Released in the United States (continued)

| Emission Source Category | Quantitative Inventory Confidence Rating ^a Reference Year 1995 | | | Quantitative Inventory Confidence Rating ^a Reference Year 1987 | | | Preliminary Estimate for 1995 ^b |
|---|---|------|---|---|------|---|--|
| | A | B | C | A | B | C | |
| Combustion Sources | | | | | | | |
| Municipal waste incineration | | | | | | | |
| Industrial wood combustion | | | | | | | |
| Medical waste incineration | | | | | | | |
| Tire combustion | | | | | | | |
| Sewage sludge incineration | | | | | | | |
| Backyard trash burning | | | | | | | |
| Total Quantified Releases to Land^c | 0 | 51.1 | 0 | 0 | 51.1 | 0 | 0 |
| <i>Releases (g TEQ_p-WHO₉₈/yr) to Products</i> | | | | | | | |
| Municipal Sludge Disposal | | | | | | | |
| Nonincinerated sludge | | 1.7 | | | 1.7 | | |
| Chemical Manufacturing/Processing Sources | | | | | | | |
| Dyes and pigments | | | | | | | |
| Total Quantified Releases to Products^c | 0 | 1.7 | 0 | 0 | 1.7 | 0 | 0 |

- ^a A = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation with High Confidence** in the **Emission Factor** and **High Confidence in Activity Level**.
- B = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation with Medium Confidence** in the **Emission Factor** and at least **Medium Confidence in Activity Level**.
- C = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation with Low Confidence** in either the **Emission Factor** and/or the **Activity Level**.
- ^b These are preliminary indications of the potential magnitude of emissions from "unquantified" sources in Reference Year 1995. These estimates were assigned a "confidence category" rating of D and are not included in the Inventory.
- ^c TOTAL reflects only the total of the estimates made in this report.

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Table 11-3. Weight Percent Concentrations of Dioxin-like PCBs in Aroclors, Clophens, and Kanechlors

| Dioxin-Like PCB Congener | IUPAC Number | Number of Samples Analyzed | Number of Detections | Mean Conc. (ND = 0) (g/kg) | TEQ _p -WHO ₉₈ Conc. (ND = 0) (mg/kg) | Mean Conc. ^a (ND = 1/2DL) (g/kg) | TEQ _p -WHO ₉₈ Conc. ^a (ND = 1/2DL) (mg/kg) |
|--|--------------|----------------------------|----------------------|---|--|---|---|
| <u>AROCLOR 1016</u> | | | | | | | |
| 3,3',4,4'-TCB | 77 | 2 | 0 | 0 | 0 | 0 | 0 |
| 3,4,4',5-TCB | 81 | 0 | -- | -- | -- | -- | -- |
| 2,3,3',4,4'-PeCB | 105 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4,4',5-PeCB | 114 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3',4,4',5-PeCB | 118 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2',3,4,4',5-PeCB | 123 | 1 | 0 | 0 | 0 | 0 | 0 |
| 3,3',4,4',5-PeCB | 126 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3',4,4',5-HxCB | 156 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3',4,4',5'-HxCB | 157 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3',4,4',5,5'-HxCB | 167 | 1 | 0 | 0 | 0 | 0 | 0 |
| 3,3',4,4',5,5'-HxCB | 169 | 2 | 0 | 0 | 0 | 0 | 0 |
| 2,2',3,3',4,4',5-HpCB | 170 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,2',3,4,4',5,5'-HpCB | 180 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3',4,4',5,5'-HpCB | 189 | 1 | 0 | 0 | 0 | 0 | 0 |
| | | | | Total TEQ _p -WHO ₉₈ = | 0 | Total TEQ _p -WHO ₉₈ = | 0 |
| | | | | Total TEQ _p -WHO ₉₄ = | 0 | Total TEQ _p -WHO ₉₄ = | 0 |
| <u>AROCLOR 1221</u> | | | | | | | |
| 3,3',4,4'-TCB | 77 | 1 | 1 | 4.00 | 0.40 | 4.00 | 0.40 |
| 3,4,4',5-TCB | 81 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3',4,4'-PeCB | 105 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4,4',5-PeCB | 114 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3',4,4',5-PeCB | 118 | 1 | 1 | 4.50 | 0.45 | 4.50 | 0.45 |
| 2',3,4,4',5-PeCB | 123 | 1 | 0 | 0 | 0 | 0 | 0 |
| 3,3',4,4',5-PeCB | 126 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3',4,4',5-HxCB | 156 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3',4,4',5'-HxCB | 157 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,3',4,4',5,5'-HxCB | 167 | 1 | 0 | 0 | 0 | 0 | 0 |
| 3,3',4,4',5,5'-HxCB | 169 | 1 | 0 | 0 | 0 | 0 | 0 |
| 2,2',3,3',4,4',5-HpCB | 170 | 0 | -- | -- | -- | -- | -- |
| 2,2',3,4,4',5,5'-HpCB | 180 | 0 | -- | -- | -- | -- | -- |
| 2,3,3',4,4',5,5'-HpCB | 189 | 1 | 0 | 0 | 0 | 0 | 0 |
| | | | | Total TEQ _p -WHO ₉₈ = | 0.85 | Total TEQ _p -WHO ₉₈ = | 0.85 |
| | | | | Total TEQ _p -WHO ₉₄ = | 2.45 | Total TEQ _p -WHO ₉₄ = | 2.45 |
| <u>AROCLOR 1242, Clophen A-30, and Kanechlor 300</u> | | | | | | | |
| 3,3',4,4'-TCB | 77 | 12 | 12 | 3.39 | 0.34 | 3.39 | 0.34 |
| 3,4,4',5-TCB | 81 | 4 | 3 | 1.81 | 0.18 | 1.83 | 0.18 |
| 2,3,3',4,4'-PeCB | 105 | 8 | 8 | 3.66 | 0.37 | 3.66 | 0.37 |
| 2,3,4,4',5-PeCB | 114 | 5 | 2 | 1.55 | 0.77 | 1.66 | 0.83 |
| 2,3',4,4',5-PeCB | 118 | 6 | 6 | 8.27 | 0.83 | 8.27 | 0.83 |
| 2',3,4,4',5-PeCB | 123 | 6 | 4 | 1.53 | 0.15 | 1.58 | 0.16 |
| 3,3',4,4',5-PeCB | 126 | 11 | 8 | 0.06 | 6.29 | 0.11 | 11.29 |
| 2,3,3',4,4',5-HxCB | 156 | 6 | 5 | 0.48 | 0.24 | 0.52 | 0.26 |
| 2,3,3',4,4',5'-HxCB | 157 | 5 | 1 | 0.004 | 0.002 | 0.11 | 0.06 |
| 2,3',4,4',5,5'-HxCB | 167 | 5 | 1 | 0.004 | 0.00004 | 0.11 | 0.001 |
| 3,3',4,4',5,5'-HxCB | 169 | 11 | 2 | 0.00002 | 0.0002 | 0.05 | 0.54 |
| 2,2',3,3',4,4',5-HpCB | 170 | 3 | 2 | 0.38 | 0 | 0.46 | 0 |
| 2,2',3,4,4',5,5'-HpCB | 180 | 2 | 1 | 0.30 | 0 | 0.43 | 0 |
| 2,3,3',4,4',5,5'-HpCB | 189 | 4 | 0 | 0 | 0 | 0 | 0 |
| | | | | Total TEQ _p -WHO ₉₈ = | 9.17 | Total TEQ _p -WHO ₉₈ = | 14.84 |
| | | | | Total TEQ _p -WHO ₉₄ = | 10.38 | Total TEQ _p -WHO ₉₄ = | 16.07 |
| <u>AROCLOR 1248, Clophen A-40, and Kanechlor 400</u> | | | | | | | |
| 3,3',4,4'-TCB | 77 | 10 | 10 | 4.56 | 0.46 | 4.56 | 0.46 |
| 3,4,4',5-TCB | 81 | 3 | 2 | 3.44 | 0.34 | 3.45 | 0.34 |
| 2,3,3',4,4'-PeCB | 105 | 6 | 6 | 7.77 | 0.78 | 7.77 | 0.78 |
| 2,3,4,4',5-PeCB | 114 | 4 | 3 | 5.06 | 2.53 | 5.07 | 2.53 |
| 2,3',4,4',5-PeCB | 118 | 5 | 5 | 19.99 | 2.00 | 19.99 | 2.00 |
| 2',3,4,4',5-PeCB | 123 | 4 | 4 | 2.12 | 0.21 | 2.12 | 0.21 |
| 3,3',4,4',5-PeCB | 126 | 8 | 6 | 0.15 | 14.51 | 0.18 | 18.26 |
| 2,3,3',4,4',5-HxCB | 156 | 5 | 5 | 1.41 | 0.70 | 1.41 | 0.70 |
| 2,3,3',4,4',5'-HxCB | 157 | 4 | 3 | 0.33 | 0.16 | 0.34 | 0.17 |
| 2,3',4,4',5,5'-HxCB | 167 | 4 | 2 | 0.25 | 0.002 | 0.26 | 0.003 |
| 3,3',4,4',5,5'-HxCB | 169 | 9 | 3 | 0.01 | 0.13 | 0.05 | 0.47 |
| 2,2',3,3',4,4',5-HpCB | 170 | 2 | 2 | 2.05 | 0 | 2.05 | 0 |
| 2,2',3,4,4',5,5'-HpCB | 180 | 1 | 1 | 2.60 | 0 | 2.60 | 0 |
| 2,3,3',4,4',5,5'-HpCB | 189 | 3 | 1 | 0.004 | 0.0004 | 0.10 | 0.01 |
| | | | | Total TEQ _p -WHO ₉₈ = | 21.83 | Total TEQ _p -WHO ₉₈ = | 25.94 |
| | | | | Total TEQ _p -WHO ₉₄ = | 23.54 | Total TEQ _p -WHO ₉₄ = | 27.64 |

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Table 11-3. Weight Percent Concentrations of Dioxin-like PCBs in Aroclors, Clophenes, and Kanechlors (continued)

| Dioxin-Like PCB Congener | IUPAC Number | Number of Samples Analyzed | Number of Detections | Mean Conc. (ND = 0) (g/kg) | TEQ _p -WHO ₉₈ Conc. (ND = 0) (mg/kg) | Mean Conc. ^a (ND = 1/2DL) (g/kg) | TEQ _p -WHO ₉₈ Conc. ^a (ND = 1/2DL) (mg/kg) |
|--|--------------|----------------------------|----------------------|---|--|---|---|
| <u>AROCLOR 1254, Clophen A-50, and Kanechlor 500</u> | | | | | | | |
| 3,3',4,4'-TCB | 77 | 12 | 9 | 0.59 | 0.06 | 0.64 | 0.06 |
| 3,4,4',5-TCB | 81 | 3 | 1 | 15.70 | 1.57 | 15.70 | 1.57 |
| 2,3,3',4,4'-PeCB | 105 | 9 | 9 | 26.68 | 2.67 | 26.68 | 2.67 |
| 2,3,4,4',5-PeCB | 114 | 6 | 3 | 15.98 | 7.99 | 16.07 | 8.04 |
| 2,3',4,4',5-PeCB | 118 | 8 | 8 | 66.30 | 6.63 | 66.30 | 6.63 |
| 2',3,4,4',5-PeCB | 123 | 5 | 5 | 5.35 | 0.53 | 5.35 | 0.53 |
| 3,3',4,4',5-PeCB | 126 | 11 | 9 | 1.23 | 122.95 | 1.26 | 125.68 |
| 2,3,3',4,4',5-HxCB | 156 | 7 | 7 | 11.22 | 5.61 | 11.22 | 5.61 |
| 2,3,3',4,4',5'-HxCB | 157 | 6 | 5 | 1.49 | 0.75 | 1.54 | 0.77 |
| 2,3',4,4',5,5'-HxCB | 167 | 7 | 6 | 2.47 | 0.02 | 2.47 | 0.02 |
| 3,3',4,4',5,5'-HxCB | 169 | 11 | 6 | 0.10 | 1.01 | 0.15 | 1.50 |
| 2,2',3,3',4,4',5-HpCB | 170 | 5 | 5 | 5.80 | 0 | 5.80 | 0 |
| 2,2',3,4,4',5,5'-HpCB | 180 | 4 | 4 | 6.63 | 0 | 6.63 | 0 |
| 2,3,3',4,4',5,5'-HpCB | 189 | 4 | 1 | 0.07 | 0.01 | 0.20 | 0.02 |
| | | | | Total TEQ _p -WHO ₉₈ = | 149.81 | Total TEQ _p -WHO ₉₈ = | 153.11 |
| | | | | Total TEQ _p -WHO ₉₄ = | 149.12 | Total TEQ _p -WHO ₉₄ = | 152.44 |
| <u>AROCLOR 1260, Clophen A-60, and Kanechlor 600</u> | | | | | | | |
| 3,3',4,4'-TCB | 77 | 12 | 6 | 0.16 | 0.02 | 0.21 | 0.02 |
| 3,4,4',5-TCB | 81 | 3 | 1 | 0.15 | 0.02 | 0.18 | 0.02 |
| 2,3,3',4,4'-PeCB | 105 | 8 | 8 | 1.56 | 0.16 | 1.56 | 0.16 |
| 2,3,4,4',5-PeCB | 114 | 6 | 3 | 1.00 | 0.50 | 1.10 | 0.55 |
| 2,3',4,4',5-PeCB | 118 | 8 | 7 | 11.13 | 1.11 | 11.13 | 1.11 |
| 2',3,4,4',5-PeCB | 123 | 5 | 1 | 0.0008 | 0.00 | 0.11 | 0.01 |
| 3,3',4,4',5-PeCB | 126 | 11 | 7 | 2.30 | 230.22 | 2.33 | 233.27 |
| 2,3,3',4,4',5-HxCB | 156 | 8 | 8 | 7.54 | 3.77 | 7.54 | 3.77 |
| 2,3,3',4,4',5'-HxCB | 157 | 5 | 5 | 2.28 | 1.14 | 2.28 | 1.14 |
| 2,3',4,4',5,5'-HxCB | 167 | 7 | 6 | 3.23 | 0.03 | 3.23 | 0.03 |
| 3,3',4,4',5,5'-HxCB | 169 | 11 | 5 | 0.21 | 2.09 | 0.24 | 2.37 |
| 2,2',3,3',4,4',5-HpCB | 170 | 5 | 5 | 28.98 | 0 | 28.98 | 0 |
| 2,2',3,4,4',5,5'-HpCB | 180 | 4 | 4 | 66.30 | 0 | 66.30 | 0 |
| 2,3,3',4,4',5,5'-HpCB | 189 | 5 | 5 | 2.16 | 0.22 | 2.16 | 0.22 |
| | | | | Total TEQ _p -WHO ₉₈ = | 239.27 | Total TEQ _p -WHO ₉₈ = | 242.66 |
| | | | | Total TEQ _p -WHO ₉₄ = | 242.88 | Total TEQ _p -WHO ₉₄ = | 246.29 |

^a Calculated for a congener only when at least one sample contained detectable levels of that congener.

References:

Schulz et al. (1989)
 Duinker and Hillebrand (1983)
 deBoer et al. (1993)
 Schwartz et al. (1993)
 Larsen, et al. (1992)
 Kannan et al. (1987)
 Huckins et al. (1980)
 Albro and Parker (1979)
 Jensen et al. (1974)
 Albro et al. (1981)
 Duinker et al. (1988)
 Tanabe et al. (1987)
 Himberg and Sippola (1990)

g/kg = grams per kilogram.
 mg/kg = milligrams per kilogram.

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Table 11-4. Disposal Requirements for PCBs and PCB Items

| | Waste Characterization | | Disposal Requirements |
|----------------|--|--|---|
| | | | |
| PCBs | Mineral oil dielectric fluids from PCB transformers | Those analyzing > 500 ppm PCB | Annex I incinerator ^a |
| | Mineral oil dielectric fluids from PCB-contaminated transformers | Those analyzing 50-500 ppm PCB | Annex I incinerator High efficiency boiler (40 CFR 761.10(a)(2)(iii)) Other approved incinerator ^b Annex II chemical waste landfill ^c |
| | PCB liquid wastes other than mineral oil dielectric fluid | Those analyzing > 500 ppm PCB Those analyzing 50-500 ppm PCB | Annex I incinerator Annex I incinerator High efficiency boiler (40 CFR 761.10(a)(2)(iii)) Other approved incinerator ^b Annex II chemical waste landfill ^c |
| | Nonliquid PCB wastes (e.g., contaminated materials from spills) | | Annex I incinerator Annex II chemical waste landfill |
| | Dredged materials and municipal sewage treatment sludges containing PCBs | | Annex I incinerator Annex II chemical waste landfill Other approved disposal method (40 CFR 761.10(a)(5)(iii)) |
| PCB Articles | Transformers | PCB transformers | Annex I incinerator Drained and rinsed transformers may be disposed of in Annex II chemical waste landfill |
| | | PCB contaminated transformers | Disposal of drained transformers is not regulated |
| | PCB capacitors | | Annex I incinerator |
| | PCB hydraulic machines | Those containing > 1,000 ppm PCB Those containing < 1,000 ppm PCB | Drained and rinsed machines may be disposed of as municipal solid waste or salvaged Drained machines may be disposed of as municipal solid waste or salvaged |
| | Other PCB articles | Those containing PCB fluids Those not containing PCB fluids | Drained machines may be disposed of per Annex I or Annex II Annex I incinerator or Annex II chemical waste landfill |
| PCB Containers | Those used to contain only PCBs at a concentration < 500 ppm | | As municipal solid waste provided any liquid PCBs are drained prior to disposal |
| | Other PCB containers | | Annex I incinerator Annex II, provided any liquid PCBs are drained prior to disposal Decontaminate per Annex IV |

^a Annex I incinerator defined in 40 CFR 761.40.

^b Requirements for other approved incinerators are defined in 40 CFR 761.10(e).

^c Annex II chemical waste landfills are described in 40 CFR 761.41. Annex II disposal is permitted if the PCB waste contains less than 500 ppm PCB and is not ignitable as per 40 CFR Part 761.41(b)(8)(iii).

^d Disposal of containerized capacitors in Annex II landfills was permitted until March 1, 1981; thereafter, only Annex I incineration has been permitted.

ppm = parts per million

Table 11-5. Off-site Transfers of PCBs Reported in TRI (1988-1996)

| Year | No. of TRI Forms Filed | Reported Transfers (kg) | | |
|------|------------------------|-------------------------|-----------------------------------|-----------------|
| | | Transfers to POTWs | Transfers for Treatment/ Disposal | TOTAL TRANSFERS |
| 1996 | NA | 0 | 160,802 | 160,802 |
| 1995 | NA | 0 | 308,347 | 308,347 |
| 1994 | NA | 0 | 466,948 | 466,948 |
| 1993 | 16 | 120 | 463,385 | 463,505 |
| 1992 | 20 | 0 | 766,638 | 766,638 |
| 1991 | 26 | 0 | 402,535 | 402,535 |
| 1990 | NA | 0 | 1,181,961 | 1,181,961 |
| 1989 | NA | 0.5 | 2,002,237 | 2,002,237 |
| 1988 | 122 | 113 | 2,642,133 | 2,642,246 |

NA = Not available

kg = kilograms

POTWs = Publicly owned treatment works

Sources: U.S. EPA (1993h), U.S. EPA (1995g), U.S. EPA (1998b)

Table 11-6. Releases of PCBs Reported in TRI (1988-1996)

| Year | No. of TRI Forms Filed | Reported Releases (kg) | | | | | |
|------|------------------------|------------------------------------|------------------------------|--------------------------|-----------------------|--------------------------|------------------------|
| | | Fugitive or Nonpoint Air Emissions | Stack or Point Air Emissions | Surface Water Discharges | Underground Injection | On-Site Releases to Land | TOTAL ON-SITE RELEASES |
| 1996 | NA | 2.3 | 114 | 0 | 0 | 4,179 | 4,295 |
| 1995 | NA | 0 | 0 | 0 | 0 | 0 | 0 |
| 1994 | NA | 0 | 0 | 0 | 0 | 0 | 0 |
| 1993 | 16 | 0 | 0 | 0 | 0 | 120 | 120 |
| 1992 | 20 | 0 | 0 | 0 | 0 | 0.5 | 0.5 |
| 1991 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1990 | NA | 2.3 | 0 | 0 | 0 | 32,372 | 32,374 |
| 1989 | NA | 0 | 0 | 120 | 0 | 453 | 573 |
| 1988 | 122 | 2.7 | 0 | 4.5 | 0 | 341 | 348 |

Sources: U.S. EPA (1993h); U.S. EPA (1995g); U.S. EPA (1998b)

NA = Not available.

Table 11-7. Aroclor Concentrations Measured in EPA's National Sewage Sludge Survey

| Aroclor | Percent Detected | Maximum Concentration (ng/kg) | Median Concentration (ng/kg) | |
|---------------------|------------------|-------------------------------|------------------------------|------------------------|
| | | | Nondetects Set to Det. Limit | Nondetects Set to Zero |
| 1016 | 0 | -- | -- | 0 |
| 1221 | 0 | -- | -- | 0 |
| 1232 | 0 | -- | -- | 0 |
| 1242 | 0 | -- | -- | 0 |
| 1248 | 9 | 5.20 | 0.209 | 0 |
| 1254 | 8 | 9.35 | 0.209 | 0 |
| 1260 | 10 | 4.01 | 0.209 | 0 |
| Any Aroclor (total) | 19 | 14.7 | 1.49 | 0 |

Source: U.S. EPA (1996a); for POTWs with multiple samples, the pollutant concentrations were averaged before the summary statistics presented in the table were calculated. All concentrations are in units of nanograms per kilogram (ng/kg) dry weight.

Table 11-8. Dioxin-Like PCB Concentrations Measured in Sludges Collected from 74 U.S. POTWs During 1994^a

| Congener | IUPAC Number | Percent Detected | Maximum Concentration (ng/kg) | Median Concentration (ng/kg) | | Mean Concentration (ng/kg) | |
|---|--------------|------------------|-------------------------------|----------------------------------|------------------------|----------------------------------|------------------------|
| | | | | Nondetects Set to 1/2 Det. Limit | Nondetects Set to Zero | Nondetects Set to 1/2 Det. Limit | Nondetects Set to Zero |
| 3,3',4,4'-TCB | 77 | 100 | 22,900 | 783 | 783 | 2,243 | 2,243 |
| 3,4,4',5-TCB | 81 | 86 | 1,250 | 27.3 | 27.0 | 65.2 | 63.5 |
| 2,3,3',4,4'-PeCB | 105 | | | | | | |
| 2,3,4,4',5-PeCB | 114 | | | | | | |
| 2,3',4,4',5-PeCB | 118 | | | | | | |
| 2',3,4,4',5-PeCB | 123 | | | | | | |
| 3,3',4,4',5-PeCB | 126 | 99 | 3,020 | 91.6 | 91.6 | 237 | 237 |
| 2,3,3',4,4',5-HxCB | 156 | | | | | | |
| 2,3,3',4,4',5'-HxCB | 157 | | | | | | |
| 2,3',4,4',5,5'-HxCB | 167 | | | | | | |
| 3,3',4,4',5,5'-HxCB | 169 | 22 | 1,470 | 8.5 | 0 | 32.5 | 26.2 |
| 2,2',3,3',4,4',5-HpCB | 170 | | | | | | |
| 2,2',3,4,4',5,5'-HpCB | 180 | | | | | | |
| 2,3,3',4,4',5,5'-HpCB | 189 | | | | | | |
| Total TEQ _p -WHO ₉₄ | | | | 9.5 | 9.5 | 25.2 | 25.1 |
| Total TEQ _p -WHO ₉₈ | | | | 9.3 | 9.2 | 24.3 | 24.2 |

ng/kg = nanograms per kilogram

- a For POTWs with multiple samples, the sample concentrations were averaged by Cramer et al. (1994) to POTW averages before calculation of the total TEQ mean and median values presented in the table. The TEQ_p-WHO₉₄ and TEQ_p-WHO₉₈ values were calculated on a facility-level basis.

NOTE: Blank cells indicate that no measurements of these congeners were made.

Source: Green et al. (1995); Cramer et al. (1995)

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Table 11-9. Dioxin-Like PCB Concentrations in Sludges Collected from a U.S. POTW During 1999

| Congener | IUPAC Number | Run 1 (ng/kg, dry) | Run 2 (ng/kg, dry) | Run 3 (ng/kg, dry) | Average Conc. (ng/kg) |
|---|--------------|-----------------------|-----------------------|-----------------------|--------------------------|
| 3,3',4,4'-TCB | 77 | 40,899 | 41,096 | 45,386 | 42,460 |
| 3,4,4',5-TCB | 81 | | | | |
| 2,3,3',4,4'-PeCB | 105 | 7,015 | 7,389 | 7,289 | 7,231 |
| 2,3,4,4',5-PeCB | 114 | 691 | 674 | 738 | 701 |
| 2,3',4,4',5-PeCB | 118 | 12,250 | 13,497 | 12,856 | 12,868 |
| 2',3,4,4',5-PeCB | 123 | 231 | 276 | 241 | 249 |
| 3,3',4,4',5-PeCB | 126 | 1,118 | 1,214 | 1,479 | 1,270 |
| 2,3,3',4,4',5-HxCB | 156 | 1,772 | 1,883 | 1,876 | 1,844 |
| 2,3,3',4,4',5'-HxCB | 157 | 472 | 565 | 536 | 524 |
| 2,3',4,4',5,5'-HxCB | 167 | 878 | 968 | 959 | 935 |
| 3,3',4,4',5,5'-HxCB | 169 | 453 | 601 | 656 | 570 |
| 2,2',3,3',4,4',5-HpCB | 170 | 2,526 | 2,572 | 2,776 | 2,625 |
| 2,2',3,4,4',5,5'-HpCB | 180 | 6,002 | 6,780 | 6,711 | 6,498 |
| 2,3,3',4,4',5,5'-HpCB | 189 | 181 | 198 | 218 | 199 |
| | | | | | |
| Total TEQ _P -WHO ₉₄ | | 141 | 152 | 181 | 158 |
| Percent due to PCBs 77, 81, 126, and 169 | | 97.3% | 97.3% | 97.8% | 97.5% |
| | | | | | |
| Total TEQ _P -WHO ₉₈ | | 124 | 135 | 163 | 141 |
| Percent due to PCBs 77, 81, 126, and 169 | | 97.2% | 97.3% | 97.8% | 97.4% |

* For POTWs with multiple samples, the sample TEQ concentrations were averaged to POTW averages before calculation of the TEQ mean and median values presented in the table.

NOTE: Blank cells indicate that no measurements of these congeners were made.

Source: Battelle (1999)

Table 11-10. Quantity of Sewage Sludge Disposed of Annually by Primary, Secondary, or Advanced Treatment POTWs and Potential Dioxin-Like PCB TEQ Releases

| Use/Disposal Practice | Volume Disposed (thousands of dry metric tons/year) | Percent of Total Volume | Potential TEQ _p -WHO ₉₈ Release ^c (g of TEQ/yr) | Potential TEQ _p -WHO ₉₄ Release ^c (g of TEQ/yr) |
|--|---|-------------------------------|---|---|
| Land Application | 1,714 | 32.0 ^e | 41.5 | 43.0 |
| Distribution and Marketing | 71 | 1.3 | 1.7 | 1.8 |
| Surface Disposal Site/Other | 396 | 7.4 | 9.6 | 9.9 |
| Sewage Sludge Landfill | 157 | 2.9 | 4.2 | 3.9 |
| Co-Disposal Landfills ^a | 1,819 | 33.9 | 44.0 | 45.6 |
| Sludge Incinerators and Co- Incinerators ^b | 865 | 16.1 | (f) | |
| Ocean Disposal | (336) ^d | (6.3) ^d | (0) ^d | |
| TOTAL | 5,357 | 100.0 | 101.0 | 104.2 |

^a Landfills used for disposal of sewage sludge and solid waste residuals.

^b Co-incinerators treat sewage sludge in combination with other combustible waste materials.

^c Potential TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (i.e., column 2) by the mean dioxin-like PCB TEQ concentration in 74 POTW sludges reported by Green et al. (1995) and Cramer et al. (1995) (i.e., 24.2 ng TEQ_p-WHO₉₈/kg and 25.1 ng TEQ_p-WHO₉₄/kg).

^d The Ocean Dumping Ban Act of 1988 generally prohibited the dumping of sewage sludge into the ocean after December 31, 1991. Ocean dumping of sewage sludge ended in June 1992 (Federal Register, 1993b). The current method of disposal of the 336,000 metric tons of sewage sludge that were disposed in the oceans in 1988 has not been determined.

^e Includes 21.9 percent applied to agricultural land, 2.8 percent applied as compost, 0.6 percent applied to forestry land, 3.1 percent applied to "public contact" land, 1.2 percent applied to reclamation sites, and 2.4 percent applied in undefined settings.

^f See Section 11.4.6 for a discussion of dioxin-like PCB releases to air from sewage sludge incinerators.

Sources: Federal Register (1990); Federal Register (1993b); Green et al. (1995); Cramer et al. (1995).

Table 11-11. PCB Congener Group Emission Factors for Industrial Wood Combustors

| Congener Group | Number of Sites | Number of Detections | Maximum Concentration Detected (ng/kg wood) | Mean Concentration (ng/kg) | |
|----------------------|-----------------|----------------------|---|------------------------------|------------------------|
| | | | | Nondetects Set to Det. Limit | Nondetects Set to Zero |
| Monochlorobiphenyls | 2 | 1 | 32.1 | 39.4 | 16.0 |
| Dichlorobiphenyls | 2 | 1 | 23.0 | 50.9 | 11.5 |
| Trichlorobiphenyls | 2 | 1 | 19.7 | 42.3 | 9.8 |
| Tetrachlorobiphenyls | 2 | 0 | -- | 22.7 | -- |
| Pentachlorobiphenyls | 2 | 0 | -- | 17.6 | -- |
| Hexachlorobiphenyls | 2 | 0 | -- | 17.0 | -- |
| Heptachlorobiphenyls | 2 | 0 | -- | 17.9 | -- |
| Octachlorobiphenyls | 2 | 0 | -- | 15.8 | -- |
| Nonachlorobiphenyls | 2 | 0 | -- | 25.0 | -- |
| Decachlorobiphenyls | 2 | 0 | -- | 36.3 | -- |

ng/kg = nanograms per kilogram.

Source: CARB (1990e, 1990f)

Table 11-12. PCB Congener Group Emission Factors for Medical Waste Incinerators (MWIs)

| Congener Group | Mean Emission Factor (ng/kg) (2 MWIs without APCD) | | Mean Emission Factor (ng/kg) (2 MWIs with APCD) | |
|----------------------|---|------------------------------|--|------------------------------|
| | Nondetects Set to Det. Limit | Nondetects Set to Zero | Nondetects Set to Det. Limit | Nondetects Set to Zero |
| Monochlorobiphenyls | 0.059 | 0.059 | 0.311 | 0 |
| Dichlorobiphenyls | 0.083 | 0.083 | 0.340 | 0 |
| Trichlorobiphenyls | 0.155 | 0.155 | 0.348 | 0 |
| Tetrachlorobiphenyls | 4.377 | 4.377 | 1.171 | 0 |
| Pentachlorobiphenyls | 2.938 | 2.938 | 17.096 | 9.996 |
| Hexachlorobiphenyls | 0.238 | 0.238 | 1.286 | 1.078 |
| Heptachlorobiphenyls | 0.155 | 0.155 | 0.902 | 0 |
| Octachlorobiphenyls | 0.238 | 0.238 | 0.205 | 0 |
| Nonachlorobiphenyls | 0.155 | 0.155 | -- | -- |
| Decachlorobiphenyls | 0.155 | 0.155 | 0.117 | 0 |

APCD = Air Pollution Control Device

ng/kg = nanograms per kilogram.

-- = Not reported.

Source: See Section 3.3 for details on tested facilities.

Table 11-13. PCB Congener Group Emission Factors for a Tire Combustor

| Congener Group | Number of Samples | Number of Detections | Maximum Emission Factor (ng/kg) | Mean Emission Factor (ng/kg) | |
|----------------------|-------------------|----------------------|---------------------------------|------------------------------|------------------------|
| | | | | Nondetects Set to Det. Limit | Nondetects Set to Zero |
| Monochlorobiphenyls | 3 | 0 | -- | 0.04 | -- |
| Dichlorobiphenyls | 3 | 1 | 34.8 | 11.7 | 11.6 |
| Trichlorobiphenyls | 3 | 1 | 29.5 | 11.8 | 9.8 |
| Tetrachlorobiphenyls | 3 | 0 | -- | 10.0 | -- |
| Pentachlorobiphenyls | 3 | 2 | 2,724 | 1,092 | 1,092 |
| Hexachlorobiphenyls | 3 | 1 | 106.5 | 55.9 | 35.5 |
| Heptachlorobiphenyls | 3 | 1 | 298.6 | 107.7 | 99.5 |
| Octachlorobiphenyls | 3 | 0 | -- | 20.9 | -- |
| Nonachlorobiphenyls | 3 | 0 | -- | 17.7 | -- |
| Decachlorobiphenyls | 3 | 0 | -- | 41.9 | -- |

ng/kg = nanograms per kilogram.

Source: CARB (1991a)

Table 11-14. Dioxin-Like PCB Concentrations in Cigarette Tobacco

| Congener | IUPAC Number | Concentrations in brands from various countries (pg/pack) | | | | | | |
|---|--------------|---|----------------------------|-------------------------------------|---------------------|--------------------|----------------------|----------------------|
| | | U.S. Brands (Avg of 7 brands) | Japan (Avg of 6 brands) | United Kingdom (Avg of 3 brands) | Taiwan (1 brand) | China (1 brand) | Denmark (1 brand) | Germany (1 brand) |
| 3,3',4,4'-TCB | 77 | 105.7 | 70.2 | 53.0 | 133.9 | 12.6 | 21.7 | 39.3 |
| 3,4,4',5-TCB | 81 | | | | | | | |
| 2,3,3',4,4'-PeCB | 105 | | | | | | | |
| 2,3,4,4',5-PeCB | 114 | | | | | | | |
| 2,3',4,4',5-PeCB | 118 | | | | | | | |
| 2',3,4,4',5-PeCB | 123 | | | | | | | |
| 3,3',4,4',5-PeCB | 126 | 6.2 | 7.8 | 6.1 | 14.5 | 2.4 | 2.2 | 7.3 |
| 2,3,3',4,4',5-HxCB | 156 | | | | | | | |
| 2,3,3',4,4',5'-HxCB | 157 | | | | | | | |
| 2,3',4,4',5,5'-HxCB | 167 | | | | | | | |
| 3,3',4,4',5,5'-HxCB | 169 | 0.9 | 0.9 | 0.9 | 2.4 | 0.4 | 0.5 | 1.6 |
| 2,2',3,3',4,4',5-HpCB | 170 | | | | | | | |
| 2,2',3,4,4',5,5'-HpCB | 180 | | | | | | | |
| 2,3,3',4,4',5,5'-HpCB | 189 | | | | | | | |
| Total TEQ _p -WHO ₉₄ | | 0.68 | 0.82 | 0.64 | 1.54 | 0.25 | 0.24 | 0.76 |
| Total TEQ _p -WHO ₉₈ | | 0.64 | 0.80 | 0.62 | 1.49 | 0.24 | 0.23 | 0.75 |

Source: Matsueda et al. (1994)

NOTE: Blank cells indicate that no measurements of these congeners were made.

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Table 11-15. Dioxin-Like PCB Concentrations in Stack Gas Collected from a U.S. Sewage Sludge Incinerator

| Congener | IUPAC Number | Run 1 (ng/dscm) (@ 7% O ₂) | Run 2 (ng/dscm) (@ 7% O ₂) | Run 3 (ng/dscm) (@ 7% O ₂) | Average Conc. (ng/dscm) (@ 7% O ₂) |
|---|--------------|--|--|--|--|
| 3,3',4,4'-TCB * | 77 | 49.20 | 38.18 | 13.26 | 33.54 |
| 3,4,4',5-TCB | 81 | | | | |
| 2,3,3',4,4'-PeCB | 105 | 5.23 | 4.32 | 1.75 | 3.77 |
| 2,3,4,4',5-PeCB | 114 | 0.76 | 0.60 | 0.25 | 0.54 |
| 2,3',4,4',5-PeCB | 118 | 11.20 | 9.27 | 4.10 | 8.19 |
| 2',3,4,4',5-PeCB | 123 | 0.23 | 0.20 | 0.07 | 0.17 |
| 3,3',4,4',5-PeCB | 126 | 1.37 | 1.03 | 0.39 | 0.93 |
| 2,3,3',4,4',5-HxCB | 156 | 1.26 | 0.99 | 0.39 | 0.88 |
| 2,3,3',4,4',5'-HxCB | 157 | 0.43 | 0.32 | 0.15 | 0.30 |
| 2,3',4,4',5,5'-HxCB | 167 | 0.76 | 0.59 | 0.25 | 0.54 |
| 3,3',4,4',5,5'-HxCB | 169 | 1.10 | 0.82 | 0.26 | 0.73 |
| 2,2',3,3',4,4',5-HpCB | 170 | 2.12 | 1.70 | 0.81 | 1.54 |
| 2,2',3,4,4',5,5'-HpCB | 180 | 5.27 | 4.18 | 1.59 | 3.68 |
| 2,3,3',4,4',5,5'-HpCB | 189 | 0.19 | 0.13 | 0.08 | 0.13 |
| | | | | | |
| Total TEQ _P -WHO ₉₄ | | 1.76E-01 | 1.33E-01 | 4.94E-02 | 1.19E-01 |
| Percent due to PCBs 77, 126, and 169 | | 98.2% | 98.1% | 97.8% | 98.1% |
| | | | | | |
| Total TEQ _P -WHO ₉₈ | | 1.56E-01 | 1.17E-01 | 4.40E-02 | 1.06E-01 |
| Percent due to PCBs 77, 126, and 169 | | 98.1% | 98.0% | 97.7% | 98.0% |

* PCB-77 concentrations were greater than the highest point on the lab's PCB calibration curve.

NOTE: Blank cells indicate that no measurements of these congeners were made.

Source: Battelle (1999)

Table 11-16. Dioxin-Like PCB Emission Factors from Backyard Barrel Burning

| Congener | IUPAC Number | Emission Factors (ug/kg) | | |
|---|--------------|--------------------------|----------|----------|
| | | Test 1 | Test 2 | Average |
| 3,3',4,4'-TCB | 77 | 9.3 | 15.2 | 12.3 |
| 3,4,4',5-TCB | 81 | | | |
| 2,3,3',4,4'-PeCB | 105 | 5.9 | 4.9 | 5.4 |
| 2,3,4,4',5-PeCB | 114 | | | |
| 2,3',4,4',5-PeCB | 118 | 8.3 | 14.3 | 11.3 |
| 2',3,4,4',5-PeCB | 123 | 18.6 | 28.7 | 23.7 |
| 3,3',4,4',5-PeCB | 126 | | | |
| 2,3,3',4,4',5-HxCB | 156 | | | |
| 2,3,3',4,4',5'-HxCB | 157 | | | |
| 2,3',4,4',5,5'-HxCB | 167 | | | |
| 3,3',4,4',5,5'-HxCB | 169 | | | |
| 2,2',3,3',4,4',5-HpCB | 170 | | | |
| 2,2',3,4,4',5,5'-HpCB | 180 | | | |
| 2,3,3',4,4',5,5'-HpCB | 189 | | | |
| Total TEQ _P -WHO ₉₄ | | 7.93E-03 | 1.24E-02 | 1.02E-02 |
| Total TEQ _P -WHO ₉₈ | | 4.21E-03 | 6.31E-03 | 5.26E-03 |

Source: Lemieux (1997)

NOTE: Blank cells indicate that the congener was not detected in either of the two duplicate samples.

Table 11-17. PCB Congener Group Emission Factors for a Petroleum Catalytic Reforming Unit

| Congener Group | Number of Samples | Number of Detections | Mean Concentration (ng/dscm) (at 12% O ₂) | Mean Emission Rate (lb/hr) | Mean Emission Factor (lb/1000bbl) | Mean Emission Factor (ng/barrel) |
|----------------------|-------------------|----------------------|---|----------------------------|-----------------------------------|----------------------------------|
| Monochlorobiphenyls | 3 | 3 | 166 | 5.51E-08 | 7.11E-09 | 3.23E+ 00 |
| Dichlorobiphenyls | 3 | 3 | 355 | 1.17E-07 | 1.52E-08 | 6.89E+ 00 |
| Trichlorobiphenyls | 3 | 3 | 743 | 2.45E-07 | 3.17E-08 | 1.44E+ 01 |
| Tetrachlorobiphenyls | 3 | 3 | 849 | 2.81E-07 | 3.62E-08 | 1.64E+ 01 |
| Pentachlorobiphenyls | 3 | 3 | 914 | 3.02E-07 | 3.88E-08 | 1.76E+ 01 |
| Hexachlorobiphenyls | 3 | 3 | 780 | 2.57E-07 | 3.30E-08 | 1.50E+ 01 |
| Heptachlorobiphenyls | 3 | 3 | 1,430 | 4.73E-07 | 6.01E-08 | 2.73E+ 01 |
| Octachlorobiphenyls | 3 | 3 | 698 | 2.32E-07 | 2.95E-08 | 1.34E+ 01 |
| Nonachlorobiphenyls | 3 | 3 | 179 | 5.99E-08 | 7.59E-09 | 3.44E+ 00 |
| Decachlorobiphenyls | 3 | 3 | 41.3 | 1.39E-08 | 1.76E-09 | 7.98E-01 |
| | | | | | | |
| Total PCBs | | | 6,155 | 2.04E-06 | 2.61E-07 | 1.18E+ 02 |

Source: CARB (1999)

Table 11-18. Estimated Tropospheric Half-Lives of Dioxin-Like PCBs with Respect to Gas-Phase Reaction with the OH Radical

| Congener Group | Dioxin-Like Congener | Estimated OH Reaction Rate Constant (10^{-12} cm ³ /molecule-sec) | Estimated Tropospheric Lifetime (days) ^a | Estimated Tropospheric Half-Life (days) ^a |
|----------------|-----------------------|---|---|--|
| TCB | 3,3',4,4'-TCB | 0.583 | 20 | 14 |
| | 3,4,4',5-TCB | 0.710 | 17 | 12 |
| PeCB | 2,3,3',4,4'-PeCB | 0.299 | 40 | 28 |
| | 2,3,4,4',5-PeCB | 0.383 | 31 | 22 |
| | 2,3',4,4',5-PeCB | 0.299 | 40 | 28 |
| | 2',3,4,4',5-PeCB | 0.482 | 25 | 17 |
| | 3,3',4,4',5-PeCB | 0.395 | 30 | 21 |
| HxCB | 2,3,3',4,4',5-HxCB | 0.183 | 65 | 45 |
| | 2,3,3',4,4',5'-HxCB | 0.214 | 56 | 39 |
| | 2,3',4,4',5,5'-HxCB | 0.214 | 56 | 39 |
| | 3,3',4,4',5,5'-HxCB | 0.266 | 45 | 31 |
| HpCB | 2,2',3,3',4,4',5-HpCB | 0.099 | 121 | 84 |
| | 2,2',3,4,4',5,5'-HpCB | 0.099 | 121 | 84 |
| | 2,3,3',4,4',5,5'-HpCB | 0.125 | 95 | 66 |

cm³ = cubic centimeters.

^a Calculated using a 24-hour, seasonal, annual, and global tropospheric average OH radical concentration of 9.7×10^5 molecule/cm³ (Prinn et al., 1995).

Source: Atkinson (1995) [Based on Atkinson (1991) and Kwok et al. (1995)].

Table 11-19. Estimated PCB Loads in the Global Environment as of 1985

| Environment | PCB Load (metric tons) | Percentage of PCB Load | Percentage of World Production |
|-----------------------------------|---------------------------|---------------------------|--------------------------------------|
| <i>Terrestrial and Coastal</i> | | | |
| Air | 500 | 0.13 | |
| River and Lake Water | 3,500 | 0.94 | |
| Seawater | 2,400 | 0.64 | |
| Soil | 2,400 | 0.64 | |
| Sediment | 130,000 | 35 | |
| Biota | <u>4,300</u> | <u>1.1</u> | |
| Total (A) | 143,000 | 39.00 | |
| <i>Open Ocean</i> | | | |
| Air | 790 | 0.21 | |
| Seawater | 230,000 | 61 | |
| Sediment | 110 | 0.03 | |
| Biota | <u>270</u> | <u>0.07</u> | |
| Total (B) | 231,000 | 61.00 | |
| Total Load in Environment (A + B) | 374,000 | 100 | 31 |
| Degraded and Incinerated | 43,000 | | 4 |
| Land-stocked ^a | <u>783,000</u> | | <u>65</u> |
| World Production | 1,200,000 | | 100 |

^a Still in use in electrical equipment and other products, and deposited in landfills and dumps.

Source: Tanabe (1988); note that a world production of 1.2-million metric tons is assumed by Tanabe (1988). DeVoogt and Brinkman (1989) estimated worldwide production to have been 1.5-million metric tons.

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Table 11-20. Domestic Sales of Aroclors (1957-1974)

| Year | Estimated Domestic Sales | | | | | | | | | Total PCB Releases (metric tons) |
|------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------------|
| | Aroclor 1016 (metric tons) | Aroclor 1221 (metric tons) | Aroclor 1232 (metric tons) | Aroclor 1242 (metric tons) | Aroclor 1248 (metric tons) | Aroclor 1254 (metric tons) | Aroclor 1260 (metric tons) | Aroclor 1262 (metric tons) | Aroclor 1268 (metric tons) | |
| 1957 | 0 | 10 | 89 | 8,265 | 807 | 2,023 | 3,441 | 14 | 0 | 14,651 |
| 1958 | 0 | 7 | 51 | 4,737 | 1,161 | 3,035 | 2,713 | 83 | 33 | 11,821 |
| 1959 | 0 | 115 | 109 | 6,168 | 1,535 | 3,064 | 3,002 | 163 | 46 | 14,202 |
| 1960 | 0 | 47 | 70 | 8,254 | 1,282 | 2,761 | 3,325 | 148 | 86 | 15,973 |
| 1961 | 0 | 43 | 109 | 8,993 | 1,825 | 2,855 | 2,966 | 164 | 72 | 17,027 |
| 1962 | 0 | 64 | 102 | 9,368 | 1,571 | 2,869 | 2,991 | 196 | 95 | 17,256 |
| 1963 | 0 | 164 | 6 | 8,396 | 2,274 | 2,681 | 3,459 | 188 | 129 | 17,296 |
| 1964 | 0 | 270 | 6 | 10,692 | 2,376 | 2,849 | 3,871 | 202 | 86 | 20,352 |
| 1965 | 0 | 167 | 3 | 14,303 | 2,524 | 3,509 | 2,645 | 253 | 89 | 23,494 |
| 1966 | 0 | 239 | 7 | 17,943 | 2,275 | 3,191 | 2,665 | 348 | 129 | 26,797 |
| 1967 | 0 | 200 | 11 | 19,529 | 2,134 | 3,037 | 2,911 | 381 | 130 | 28,334 |
| 1968 | 0 | 62 | 41 | 20,345 | 2,220 | 4,033 | 2,382 | 327 | 127 | 29,536 |
| 1969 | 0 | 230 | 124 | 20,634 | 2,563 | 4,455 | 2,013 | 323 | 136 | 30,479 |
| 1970 | 0 | 670 | 118 | 22,039 | 1,847 | 5,634 | 2,218 | 464 | 150 | 33,140 |
| 1971 | 1,512 | 1,005 | 78 | 9,970 | 97 | 2,114 | 782 | 0 | 0 | 15,559 |
| 1972 | 9,481 | 78 | 0 | 330 | 366 | 1,585 | 138 | 0 | 0 | 11,978 |
| 1973 | 10,673 | 16 | 0 | 2,812 | 0 | 3,618 | 0 | 0 | 0 | 17,119 |
| 1974 | 9,959 | 26 | 0 | 2,815 | 0 | 2,805 | 0 | 0 | 0 | 15,605 |
| TOTALS | 31,625 | 3,412 | 924 | 195,596 | 26,856 | 56,120 | 41,525 | 3,255 | 1,307 | 360,620 |
| % of Total | 8.8% | 0.9% | 0.3% | 54.2% | 7.4% | 15.6% | 11.5% | 0.9% | 0.4% | 100.0% |

Source: Versar (1976)

Table 11-21. Estimated U.S. Usage of PCBs by Use Category (1930-1975)

| Use Class | Use Category | Amount Used (1,000 metric tons) | Percent of Total Usage | Reliability of Estimate |
|---------------------------------|------------------------------|---------------------------------------|---------------------------|----------------------------|
| Closed Electrical Systems | Capacitors | 286 | 50.3 | ± 20% |
| | Transformers | 152 | 26.8 | ± 20% |
| Semi-Closed Applications | Heat transfer fluids | 9 | 1.6 | ± 10% |
| | Hydraulics and lubricants | 36 | 6.3 | ± 10% |
| Open-End Applications | Plasticizer uses | 52 | 9.2 | ± 15% |
| | Carbonless copy paper | 20 | 3.5 | ± 5% |
| | Misc. industrial | 12 | 2.1 | ± 15% |
| | Petroleum additives | 1 | < 1 | ± 50% |
| TOTAL | | 568 | 100 | |

Source: Versar (1976)

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Table 11-22. Estimated Direct Releases of Aroclors to the U.S. Environment (1930-1974)^a

| Year | Estimated Environmental Releases | | | | | Total PCB Releases (metric tons) |
|------------|----------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------------|
| | Aroclor 1016 (metric tons) | Aroclor 1242 (metric tons) | Aroclor 1248 (metric tons) | Aroclor 1254 (metric tons) | Aroclor 1260 (metric tons) | |
| 1930-56 | 0 | 8,486 | 2,447 | 2,269 | 1,614 | 14,817 |
| 1957 | 0 | 903 | 319 | 307 | 423 | 1,952 |
| 1958 | 0 | 649 | 483 | 416 | 355 | 1,903 |
| 1959 | 0 | 1,042 | 724 | 518 | 507 | 2,792 |
| 1960 | 0 | 1,340 | 556 | 449 | 540 | 2,885 |
| 1961 | 0 | 1,852 | 792 | 587 | 611 | 3,841 |
| 1962 | 0 | 1,811 | 659 | 554 | 571 | 3,594 |
| 1963 | 0 | 1,655 | 935 | 529 | 682 | 3,801 |
| 1964 | 0 | 2,085 | 980 | 555 | 755 | 4,375 |
| 1965 | 0 | 2,689 | 1,025 | 660 | 497 | 4,872 |
| 1966 | 0 | 3,180 | 876 | 566 | 472 | 5,094 |
| 1967 | 0 | 3,376 | 814 | 525 | 504 | 5,219 |
| 1968 | 0 | 3,533 | 853 | 733 | 433 | 5,552 |
| 1969 | 0 | 4,165 | 993 | 985 | 452 | 6,596 |
| 1970 | 0 | 4,569 | 697 | 1,168 | 474 | 6,907 |
| 1971 | 76 | 1,466 | 51 | 325 | 121 | 1,963 |
| 1972 | 474 | 22 | 0 | 104 | 9 | 135 |
| 1973 | 534 | 141 | 0 | 181 | 0 | 322 |
| 1974 | 498 | 141 | 0 | 140 | 0 | 281 |
| | | | | | | |
| TOTALS | 1,582 | 43,103 | 13,205 | 11,572 | 9,019 | 76,898 |
| % of Total | 2.1% | 56.1% | 17.2% | 15.0% | 11.7% | 100.0% |

a Does not include an additional 132,000 metric tons estimated to have been landfilled during this period.

Source: Versar (1976)

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Table 11-23. Estimated Releases of Dioxin-Like PCB TEQs to the U.S. Environment During 1930-1977

| Aroclor | Percent of U.S. Sales ^a (1957-1974) | Estimated PCB Releases (1930-1974) ^b (metric tons) | Estimated Mean TEQ _p -WHO ₉₈ Concentration ^c (mg/kg) | Estimated Total TEQ _p -WHO ₉₈ Released (kilograms) |
|--------------|--|---|---|--|
| Aroclor 1016 | 12.88% | 1,582 | d | d |
| Aroclor 1221 | 0.96% | -- | 0.85 | -- |
| Aroclor 1232 | 0.24% | -- | -- | -- |
| Aroclor 1242 | 51.76% | 43,103 | 9.17 | 395 |
| Aroclor 1248 | 6.76% | 13,205 | 21.83 | 288 |
| Aroclor 1254 | 15.73% | 11,572 | 149.81 | 1,733 |
| Aroclor 1260 | 10.61% | 9,019 | 239.27 | 2,158 |
| Aroclor 1262 | 0.83% | -- | -- | -- |
| Aroclor 1268 | 0.33% | -- | -- | -- |
| | | | | Total= 4,574 |

μg/kg = micrograms per kilogram.

--" indicates that release estimates were not been made because of relatively low usage amounts.

^a Sales during the period 1957-1974 constitute 63% of all PCB sales during 1930-1977; sales data for individual Aroclors are not available for years prior to 1957. However, sales of Aroclors 1221, 1232, 1262, and 1268 were minor even prior to 1957.

^b From Table 11-22.

^c From Table 11-3 (assumes not detected values are zero).

^d Data are available for only one sample of Aroclor 1016; no dioxin-like PCB congeners were detected.

Source: Versar (1976)